# LIQUID - LIQUID PHASE EQUILIBRIA

A THESIS

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LIQUID - LIQUID PHASE EQUILIBRIA

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Was sich ueberhaupt sagen laesst

laesst sich klar sagen;

und wovon man nicht reden kann,

darueber muss man schweigen.

Ludwig Wittgenstein

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## NOMENCLATURE AND DEFINITION OF TERMS

In the absence of a universally accepted system of notation for thermodynamic quantities, individual authors have the responsibility of making a choice whenever the existing systems are in conflict. The initiate in the field usually follows the notation of a text from which he has studied or uses standards set up by some professional society. With several exceptions, this paper will follow the notations used by I. Prigogine and R. Defay in their book, Chemical Thermodynamics, translated by D. H. Everett (20).

In the study of ternary liquid equilibrium, several terms need to be clearly defined. The following is a list of such terms with their meaning as determined by this author. This list is by no means complete, and for an extended discussion the reader should refer to standard texts such as Treybal (8).

immiscibility: A term used to describe the phenomenon of two phases occurring when different liquids are mixed together. An immiscible solution is also known as a heterogeneous solution.

critical solution temperature: Certain two phase liquid systems exhibit a phenomenon of increasing mutual solubility as the temperature is raised or lowered under isobaric conditions, until the second phase disappears. This phenomenon, occurring below the boiling point and above the freezing point of the system, is also known as the consolute temperature.

triangular coordinates: An equilateral triangle is used for representing compositions of ternary systems, since it can be shown that the sum of the perpendiculars from any point within the triangle to the three sides equals the altitude. The vertices, of course, represent the pure constituents of the ternary mixture.

ternary solubility curve: This is a graphical depiction of the boundary of a region of heterogeneity of a ternary mixture considering all the possible combinations of compositions,

with each point on this curve representing the composition of one of the phases. This curve is also known as the coexistence curve or the binodal curve.

tie line or conjugate line: This is a graphical depiction of the equilibrium composition of two liquid phases in mutual contact. When given a mixture whose total composition is within the solubility curve (see above), then there exists a unique conjugate line such that the composition of each phase is determinable from both intersections of the conjugate line and the ternary solubility curve.

plait point: Inasmuch as tie lines depict two equilibrium liquid phases, it often occurs that as the concentration of one component increases the tie lines "shrink." That is to say, the composition difference between the two phases gets smaller until a point is reached where the compositions of the two phases become identical. Such a point is known as the plait point.

Gibbs free energy surface: This is a three-dimensional representation of the Gibbs molal free energy as a function of the independent mole fraction compositions for a ternary system. Since the sums of the molal compositions must equal one, specifying any two will always determine the third. Immiscible systems are said to be unstable and are represented by a surface which is convex-concave.

spinodal curve: This is the boundary which separates that part of the Gibbs free energy surface which is convex from that which is concave. The spinodal curve is generally within the solubility curve, and it is tangent to the solubility curve at the plait point.

distribution curve: This is a graphical representation devised for the purpose of correlating ternary data. It consists of plotting the ratio of the concentration of component (A) to the concentration of component (B) in the B-rich phase against the ratio of the concentration of component (A) in the concentration of component (C) in the C-rich phase as determined from tie-line data. If the distribution curve is a straight line, the data are reported in terms of the distribution coefficients which represent that slope of the distribution curve. This only occurs at low concentrations of component (A).

# LIST OF SYMBOLS

| | |
|---|---|
| $a_i$ | activity of component i |
| B, B(T) | second virial coefficient in liters/gram-mole |
| c | number of components |
| d | symbol for differentiation |
| e | base of natural logarithms |
| G | Gibbs free energy |
| $G^m$ | Gibbs free energy of mixing |
| $g^m$ | Gibbs molal free energy of mixing |
| $g^E$ | excess Gibbs free energy |
| $g^{m,id}$ | Gibbs free energy of mixing of an ideal solution |
| H | ethalpy or heat content function |
| h | enthalpy per mole |
| $h_i$ | partial molar enthalpy of component i |
| $h^E$ | excess enthalpy or heat of mixing |
| i | as a subscript refers to a generalized component |
| j | as a subscript refers to a second generalized component |
| ln | natural logarithm |
| log | logarithm to the base 10 |
| $M_i$ | molecular weight of component i |
| n | total number of moles |
| $n_i$ | number of moles of component i |
| $n^a$ | number of moles in phase a |
| $n_i^a$ | number of moles of component i in phase a |

| | |
|---|---|
| $P$ | total pressure of a system |
| $p_i$ | partial pressure of component i |
| $p_i^o$ | vapor pressure of pure component i |
| $R$ | gas constant |
| $R_{12}$ | equivalent to $2B_{12}(t) - B_{11}(t) - B_{22}(t)$ |
| $s$ | entropy |
| $T$ | absolute temperature in degrees Kelvin |
| $T_c$ | critical temperature in degrees Kelvin |
| $t$ | temperature in degrees centigrade |
| $V$ | volume |
| $v$ | molar volume |
| $v_i$ | partial molar volume of component i |
| $v_i^o$ | molar volume of pure component i |
| $x_i$ | mole fraction of component i |
| $z$ | volume fraction |

GREEK ALPHABET

| | |
|---|---|
| $\gamma_i$ | activity coefficient of component i |
| $\partial$ | symbol for partial differentiation |
| $\mu_i$ | chemical potential of component i |
| $\mu_i$(ideal) | ideal chemical potential of component i |
| $\mu_i^o$ | chemical potential of component i in the pure state |
| $\mu_i^a$ | chemical potential of component i in phase a |
| $\mu_i^m$ | chemical potential of mixing |
| $\Sigma$ | symbol for summation |
| $\rho_i$ | density of pure component i in grams per liter |

(number) denotes a reference to the bibliography. Denotes an equation number of the word equation precedes this symbol.

# SUMMARY

This research was undertaken to ascertain the applicability of a general equation, which was proposed by Kurt Wohl, to the prediction of liquid-liquid phase equilibria of ternary systems from a knowledge of the equilibrium properties of the component binary systems. A second purpose was to formulate a systematic treatment of binary isothermal vapor-liquid equilibrium data. The objectives of this treatment were to be able to represent the experimental data with a high degree of accuracy and to determine whether the data are thermodynamically consistent.

This study of these objectives has been developed with the aim of presenting some of the essential steps in some future integrated process for the treatment of binary equilibrium data with the extension to the prediction of the properties of multi-component systems. The selection of the mathematical model for the activity coefficients is all that is required. More important, though, the concept of numerical experimentation is presented. A mathematical model of a high degree of complexity can be postulated and then numerically tested to find its favorable points and its shortcomings.

The model used in this study was a general equation proposed by Wohl which was basically a truncated power series expansion of the Gibbs excess free energy function in terms of liquid compositions and undetermined parameters. Rearrangement of terms as shown by Wohl (3) and partial

differentiation with respect to the mole numbers yielded a set of equations for the logarithms of the activity coefficients as functions of the liquid compositions and parameters. These equations were written in such a manner that transitions between different equational forms were easily made. Specifically the equational forms proposed by J. J. van Laar, M. Margules, and G. Scatchard and W. Hamer were studied in this work. The transition of these equations between binary and ternary systems was easily accomplished.

A literature survey was made to collect the data for ternary systems and their component binary systems. Specifically the data which was desired were:

1. Isothermal vapor-liquid equilibrium data for a partially miscible ternary system.

2. Isothermal liquid-liquid equilibrium data for the same ternary system.

3. Isothermal vapor-liquid equilibrium data for all of the component binary systems.

Since the desired data, which would permit a more systematic study of the liquid systems were not available for any ternary system, the data were collected solely on the basis of availability. In addition, liquid-liquid equilibrium data were experimentally determined for two ternary hydrocarbon systems. They are the nitroethane--n-octane--isooctane and nitroethane--n-octane--octene-1 systems.

The binary data were classified according to the following groupings:

1. Ideal binary systems.

2. Partially miscible binary systems.

3. Non-ideal miscible binary systems.

The binary data were used to compute the parameters of the binary forms of the van Laar, Margules, and Scatchard-Hamer equations. For the data of group 1 above, the parameters were set equal to zero. The parameters of the partially miscible binary systems were computed from mutual solubility data since vapor-liquid equilibrium data in the homogeneous regions were not available. From vapor-liquid equilibrium data for group 3, the parameters of the various equations were determined by the method of least squares from a fit of the data in the form of activity coefficients as functions of liquid compositions. These parameters were then used in the ternary forms of the binary equations to predict the liquid-liquid equilibria of the ternary systems whose data were available in the literature. The constants which only referred to the ternary system were set equal to zero.

The prediction scheme was basically a method of trial-and-error search using a digital computer for all the computations. The fact that at a prescribed standard state of the temperature and pressure of the system, the activities of each component in each phase are equal, when the system is at equilibrium, formed the basis for the method. Using the different equational forms for the activity coefficients, one at a time, the activities of each component were computed for many compositions in the vicinity of the guessed phase compositions. A table of these activities was built up. This guess was initially based upon the binary mutual solubility data. The activities of each component for compositions in the neighborhood of the other phase compositions were then

computed and a comparison was made with the values in the table. To automate this scheme, a quantity called D, which was the sum of the squares of the differences of the activities of each component in each phase, was computed. If this computed quantity, D, was less than some prescribed value, a possible answer was found. The final answer was the predicted conjugate phase compositions for which the D was the smallest. This scheme was then repeated to find other conjugate phase compositions or tie-line compositions.

The computed values of these tie-line or conjugate phase compositions were then compared with the experimental data of the ternary systems. The locus of the compositions of the solubility curve as determined from the computed tie-line values was compared with the experimentally determined compositions. The slopes of the computed tie-lines were compared with the experimentally determined tie-lines to determine the adequacy of predicting distribution curves for the ternary systems.

This procedure was carried out for the following ternary systems:

1. Furfural--n-heptane--cyclohexane
2. Aniline--n-heptane--cyclohexane
3. Nitroethane--n-octane--isooctane
4. Nitromethane--n-heptane--benzene
5. Benzene--water--pyridine
6. Benzene--water--ethanol
7. Chloroform--water--ethanol
8. Decyl alcohol--nitromethane--ethylene glycol

A second important phase of this research was the method developed for the treatment of binary isothermal vapor-liquid equilibrium data. The

experimental values of the total pressure and vapor compositions as functions of the liquid compositions, which were taken from the literature, were fitted in a least squares sense by orthogonal polynomials, applying the method developed by G. Forsythe, to any desired degree. The main deviation from presently used techniques is that the experimental quantities of total pressure and vapor composition are fitted by orthogonal polynomials instead of the usually computed activity coefficients or excess chemical potentials which are indeterminate at the end-points. At the end-points the total pressures and vapor compositions are known to a high degree of accuracy and thus interpolated values of these quantities can be used to compute fairly accurate values of the excess chemical potentials in the dilute composition regions. Furthermore, the method of Forsythe was extended to the computation of the derivatives of each of the fitting functions.

Since least squares theory cannot specify the degree of the best fitting polynomial, some additional condition must be found if one is to adequately represent experimental data by fitting functions. In the treatment of isothermal vapor-liquid equilibrium data, this additional condition was developed in the following manner. Assuming that the contribution of the volume change on mixing was negligible, the Gibbs-Duhem equation for the excess chemical potentials was rewritten in terms of total pressures, vapor and liquid compositions, second virial coefficients, and molal volumes and vapor pressures of each pure component. The use of this form of the Gibbs-Duhem equation provided the additional criterion needed to ascertain the best degree of fitting polynomial. The procedure was to compute a value, which was the sum of squares of the

deviations of the Gibbs-Duhem equation from zero, for every combination of fitting polynomials for the total pressures and vapor compositions. Those polynomials which exhibited the smallest computed value were said to represent the experimental data in the best possible manner with respect to thermodynamic consistency.

The following conclusions were drawn from this investigation:

1. For ternary systems containing two partially miscible binary pairs and an ideal binary pair, the liquid-liquid phase equilibria was satisfactorily predicted using the Margules model, the predictions being only slightly better than the van Laar model. The predicted distribution was very nearly the same as the experimentally determined distribution, and the predicted binodal curve followed the experimental binodal curve very closely. This conclusion was based on the results of the following systems:

Furfural--n-heptane--cyclohexane

Aniline--n-heptane--cyclohexane

Nitroethane--n-octane--isooctane

2. For ternary systems containing three immiscible binary pairs, it was possible for the Margules and van Laar equations to predict three separate binodal curves. This observation was based upon studies of the one system, decyl alcohol--nitromethane--ethylene glycol. The results of this system were quantitatively poor but nevertheless indicated the presence of three binodal curves.

3. For ternary systems containing one immiscible binary system and two non-ideal miscible binary systems, the phase composition

predictions were good for the distribution curves where the composition of the third miscible component was small. The predicted tie-lines in the concentrated regions of the ternary system were not satisfactory, in that, in all cases the predicted system was less ideal than the actual system. These conclusions were based on the results for the following four systems:

Benzene--water--pyridine

Benzene--water--ethanol

Chloroform--water--acetone

Nitromethane--n-heptane--benzene

4. The use of orthogonal polynomials provided a means of fitting experimental data to any desired degree up to the number of data points less two. The total pressures and the vapor compositions were fitted just as one would fair a curve through the data points on a graph. This is contrasted to the fact that the use of ordinary polynomials does not give good fits to vapor-liquid equilibrium data.

5. On the basis of the results of five isothermal binary systems, the test of thermodynamic consistency presented in this thesis provides a very accurate test for the evaluation of isothermal binary vapor-liquid equilibrium data. Its use is recommended over the integral tests when very accurate results are desired.

6. On the basis of the results of evaluating the parameters to the standard binary equations, discussed in this thesis, for nine non-ideal miscible systems, it was observed that the Margules three constant equation gave the best fit of the activity coefficient data in the least squares sense.

# CHAPTER I

## INTRODUCTION TO PROBLEM

The problem in a general sense.--In the highly competitive chemical industry, the success or failure of a new operation is frequently dependent upon the accuracy of equilibrium data. Whether or not to gamble an industry's assets on a new operation may be a function of the available data or the ease with which it may be obtained. In the case of liquid-liquid extraction processes, the data are frequently either not available or are difficult to obtain. Thus the question naturally arises: can existing data be used to extend or predict the state of liquid mixtures at equilibrium? If some reliable method could be found to extend or predict the equilibrium state of liquid mixtures, it is felt that among the virtually infinite combinations of chemical compounds, many important extractive processes are waiting to be discovered. Specifically, there is a need to be able to predict, quantitatively, the state of ternary liquid mixtures under conditions of phase equilibrium.

If one can successfully predict a state function such as Gibbs free energy of mixing, then one can ascertain the state of liquid mixtures in equilibrium. The Gibbs free energy of mixing can be represented as a function of the three state variables -- temperature, pressure, and the concentration of the components of the system. (Usually one does not take into account other state variables such as electrical, magnetic, capillary, or gravitational forces.) Classical thermodynamics will not tell us how to accomplish this, but it will give us the necessary relationships

between the state variables of volume, pressure, temperature and concentration.

J. Willard Gibbs, in his celebrated memoir, "On the Equilibrium of Heterogeneous Substances," stated the conditions of thermodynamic equilibrium in a form which has not been surpassed in its generality. The work of Gibbs was essentially theoretical and its full importance was appreciated only after its wide applicability had been demonstrated by extensive experimental researches. Among those was the work of Bakhuis Roozeboom on the applications of the Phase Rule. Also Planck, van Laar, Duhem and van der Waals demonstrated the importance of the concept of Gibbs' work.

Further progress was made with the introduction of the concept of fugacity and activity by G. N. Lewis, enabling the thermodynamic description of imperfect gases and of real solutions to be expressed with the same formal simplicity as perfect gases and ideal solutions. Furthermore, Scatchard's introduction of the term, excess function (1), enables one to discuss specifically the effects caused by deviations from the perfect gases and ideal solutions in a simple manner.

Thus while classical thermodynamics can only guide us, the answer to the question of obtaining numerical values for the state function will have to come from a study of the intermolecular forces which, for the liquid state, is still in the embryonic stage. Therefore, since we cannot expect anything but the crudest values even for simple systems, we must make the fullest possible use of all the relationships given to us by classical thermodynamics.

Purpose of this investigation.--It is the purpose of this research to investigate the applicability of several mathematical models for the Gibbs free energy function to the prediction of the equilibrium state of ternary liquid mixtures. Since the systems which will be discussed are at relatively low temperatures when compared to the normal boiling points of the pure components, and ternary vapor-liquid equilibrium data are not generally available, ternary vapor-liquid equilibrium will not be studied. However, the applicability of the binary vapor-liquid equilibrium data to the ternary systems will be considered.

Many people have tried to explain the properties of binary systems from the properties of the pure components. This is equivalent to predicting (1-2) interactions (i.e., interactions between components 1 and 2) from the interactions of pure components (1-1) and (2-2). This, however, has been shown not to be possible (2). Therefore, at the present time, the only certain method of obtaining the binary properties is to experimentally determine them.

It is conceivable that a binary interaction is not significantly affected by the presence of the other binary pairs which form a ternary system. In other words, the ternary properties, in terms of interactions, may be nearly equal to the sums of the interactions of the three binary pairs when considered separately. This is because the energy of an array of, say, three molecules (1-2-3), is nearly equal to the sum of the energies of the three interacting pairs (1-2), (2-3), and (1-3) when considered separately (2). Therefore, it may be possible to predict the properties of a multi-component mixture from a knowledge of the properties of all the binary mixtures.

The main purpose of this investigation is to determine if it is possible to predict the state of a ternary mixture in equilibrium by the use of binary equilibrium data. The model for the excess free energy which will be studied is one proposed by Wohl (3), who has effectively demonstrated the interrelationships between equations proposed by van Laar (4), Margules (5) and Scatchard-Hamer (6). Equilibrium data for binary systems, from the published literature, will be correlated to a binary form of the excess free energy model. The correlation constants for three constituent binary pairs will be used in the ternary excess free energy equations, which is simply an extension of the binary case, to predict the binodal curve and the tie-lines in a ternary liquid mixture. These predicted results will then be compared with ternary liquid-liquid solubility data for agreement in compositions at the liquid-liquid interface and in the slopes of the tie-lines.

Historical background.--Perhaps the first serious attempt to predict ternary data was the work of Hildebrand (7) which has been discussed in detail by Treybal (8). If one denotes the activity coefficients of component one in solvents two and three as $\gamma_{12}$ and $\gamma_{13}$, respectively, and $x_{12}$ and $x_{13}$ as the mole fractions of component one in the liquid phases, composed mainly of components two and three, respectively, then the method used by Hildebrand was to plot $\gamma_{12}\, x_{12}$ against $x_{12}$ and $\gamma_{13}\, x_{13}$ against $x_{13}$ on the same graph. From the same ordinate, values of $x_{12}$ and $x_{13}$ as abscissas are read from the two curves. This method is at best only an approximation if the mutual solubility of components one and two becomes appreciable. Furthermore, only the distribution coefficients are evaluated by this method. Treybal (8) extended Hildebrand's

concept to the case where the solubility curve of the ternary system, but without tie-lines, is available. This method is discussed elsewhere by Treybal (9). He has shown how a set of two parameter equations, whose development is attributed to van Laar and henceforth will be known as the van Laar equations, can be used to predict the distribution of a solute between two immiscible solvents. In effect, the complete ternary equilibrium state (including tie-lines) can be "predicted" if the ternary solubility curve, without tie-lines, is available. This method gives a fairly accurate description of the region dilute in the solute, but usually fails as the concentration of the solute increases.

Othmer and Tobias (10) describe a method of predicting the distribution of a solute between two immiscible solvents based on partial pressure data for the two binary solutions formed with the solute and the two solvents. Kenny (11) studied the prediction of the system furfural-isooctane-benzene using the two parameter van Laar equations, the methods of Hildebrand (7) and of Scheibel and Friedland (12). No ternary data are given, and the method is discussed in generalities so that a proper evaluation of the method used cannot be made. The use of Colburn's extrapolation method for binary systems (13), which permits the computation of the activity coefficients from the total pressure, is extended to ternary systems by Buchholz-Meissenheimer (14).

A method of predicting distribution coefficients for ternary systems with two immiscible binary pairs has been proposed by Vriens and Medcalf (15), Pennington and Marwil (16) and Bethea (17). A method for the computation of the spinodal curve for a ternary liquid mixture has been discussed by Meijering (18), (19), and Prigogine (20).

Prediction methods of ternary vapor-liquid equilibria data have been proposed by numerous authors. Among these are Scheibel and Friedland (12), Carlson and Colburn (13), Colburn and Schoenborn (21), White (22), Benedict, et al. (23), Herrington (24), Black (25), Hirata (26), Severns, et al. (27), and Li and Coull (28). All of the above methods are essentially empirical mathematical treatments of the problem of evaluating ternary vapor-liquid equilibrium data from the constituent binary data. The applicability of these equations to liquid-liquid systems has not been fully investigated, due to the complexity of the numerical computations involved. Wohl (3), (29), has presented these equations in a general manner which will form the basis for the present investigation.

This work is presented in two parts. Part one is concerned with the prediction of ternary liquid equilibrium from binary equilibrium data. Chapter II presents some basic thermodynamic relations using chemical potentials with a transition to binary and ternary equations in terms of activity coefficients. Chapter III develops the procedure for using the previously discussed equations in the prediction of ternary equilibrium data. In Chapter IV the computed results are compared with data in the literature and measurements made in this work.

Part two is concerned with the question of thermodynamic consistency of binary equilibrium data. In Chapter V, the relations are developed for the treatment of the binary data. In Chapter VI, the procedure and its ramifications are discussed with regard to thermodynamic consistency.

The conclusions of this entire work and recommendations for further studies are found in Chapter VII. The Appendices are referred to from both parts of this thesis.

# PART I. THE PREDICTION OF TERNARY LIQUID-LIQUID EQUILIBRIUM

## CHAPTER II

## DEVELOPMENT OF THERMODYNAMIC RELATIONS

Scope of this chapter.--This chapter contains a review and a development of many of the relations used in this research. Although many of the thermodynamic relations are certainly not new, they are nevertheless presented here for two reasons. First, the relations which are used are collected in one place, and secondly, the relations are given in the notation used in this thesis. These thermodynamic relations can be found in many textbooks dealing with classical thermodynamics. A few of the references cited are:

A. Prigogine and Defay, R., Chemical Thermodynamics, (translated by Everett, D. H.), Volume 1, London: Longmans, Green, and Company, Inc., 1954.

B. Dodge, B. F., Chemical Engineering Thermodynamics, New York: McGraw-Hill Book Company, Inc., 1944.

C. Guggenheim, E. A., Thermodynamics, 2nd Edition, Amsterdam: North Holland, 1957.

The first part of this chapter deals with some of the fundamental thermodynamic relationships. This is followed by an exposition of the ternary equations and their transformations to the binary equations.

Fundamental thermodynamic relations.--It is the purpose of this section to review some of the thermodynamic relations needed in the analysis of a model for the free energy of a ternary system. Some of the fundamental relations are presented.

The Gibbs free energy function, G, is an extensive function whose value is dependent on the total quantity of matter present in the system. If one writes,

$$G = G(T, P, n_1, n_2, \cdots n_c) \tag{1}$$

giving the dependent variable G as a function of the independent variables, T, P, $n_1$, $n_2$, ..., $n_c$, then one can say that it has been observed that

$$kG = G(T, P, kn_1, kn_2, \cdots kn_c) \tag{2}$$

which expresses the fact that G is a homogeneous function of the first degree in the mole numbers. The chemical potential of component i is defined by

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_j(j\neq i)} \tag{3}$$

which is the partial molal quantity corresponding to the Gibbs free energy G. It is noted that $\mu_i$ is an intensive quantity. Thus one can speak of the chemical potential of a component at each point of the system, just as one speaks of the concentrations in mole fractions. Thus we have

$$G = n_1\mu_1 + n_2\mu_2 + \cdots + n_c\mu_c = \sum_{i=1}^{c} n_i\mu_i \tag{4}$$

which upon differentiation gives

$$dG = \sum_{i=1}^{c} n_i d\mu_i + \sum_{i=1}^{c} \mu_i dn_i \qquad (5)$$

when compared with

$$dG = -SdT + VdP + \sum_{i=1}^{c} \mu_i dn_i \qquad (6)$$

one obtains

$$SdT - VdP + \sum_{i=1}^{c} n_i d\mu_i = 0. \qquad (7)$$

At constant temperature and pressure, equation (7), which may be called the most general form of the Gibbs-Duhem equation, reduces to

$$\sum_{i=1}^{c} n_i d\mu_i = 0 . \qquad (8)$$

Equation (8) is known as the Gibbs-Duhem equation and is the basis of thermodynamic consistency tests. This equation also follows from the fact that G is a homogeneous function of degree one in the mole numbers.

J. Willard Gibbs has shown that at constant temperature and pressure, a system, which may consist of more than one phase, is at equilibrium when the change in the total free energy is zero (30). Thus if one accepts that equation (6) can be written for any system, however complex, without rigorous proof, then it can be easily demonstrated that the chemical

potential of each component must be the same in every phase (31). For a closed system, the total mass of each component remains constant. This fact is given by equation (9).

$$\sum_{i=1}^{c} dn_i = 0 \tag{9}$$

Thus using the fact $dG = 0$ at equilibrium, one obtains equation (10) from equation (5).

$$\sum_{i=1}^{c} \mu_i dn_i = 0 \tag{10}$$

This equation when compared with equation (9), yields the necessary and sufficient conditions for phase equilibrium in terms of chemical potentials for a closed system in equation (11).

$$\mu_i^a = \mu_i^b = \ldots = \mu_i^z \quad (i = 1, 2, \ldots, c) \tag{11}$$

For a multicomponent mixture, the Gibbs free energy of mixing at constant temperature and pressure can be written as follows,

$$G^m = G(T, P, n_1, \ldots, n_c) - \sum_{i=1}^{c} G_i^o (T, P, n_i) . \tag{12}$$

The superscript $^o$ refers to the pure quantities. Since

$$G^m = g^m \sum_{i=1}^{c} n_i , \tag{13}$$

in terms of molar quantities one obtains,

$$g^m = g(T, P, x_1, \ldots, x_c) - \sum_{i=1}^{c} x_i g_i^{\circ}(T, P). \qquad (14)$$

The free energy of mixing is also related to the chemical potential by equation (15).

$$g^m = \sum_{i=1}^{c} x_i \mu_i - \sum_{i=1}^{c} x_i \mu_i^{\circ} . \qquad (15)$$

The chemical potential of mixing for a pure component i at constant temperature and pressure is defined by

$$\mu_i^m = \mu_i - \mu_i^{\circ} \qquad (i = 1, 2, \ldots, c). \qquad (16)$$

An ideal solution can be defined by (20),

$$\mu_i = \mu_i^{\circ} + RT \ln x_i \qquad (i = 1, 2, \ldots, c) \qquad (17)$$

From equations (16) and (17), for an ideal solution,

$$\mu_i^m = RT \ln x_i \qquad (i = 1, 2, \ldots, c). \qquad (18)$$

Deviations from the laws of ideal solutions may be expressed formally by introducing the activity coefficients $\gamma_i$ in the expression for the chemical potentials of a perfect solution. The method originated by G. N. Lewis (32) permits one to formally extend the properties of ideal solutions to actual solutions in a most elegant way. The chemical potential now takes the form

$$\mu_i(\text{real}) = \mu_i^{\circ}(T, P) + RT \ln (x_i\gamma_i) \quad (i = 1, 2, \ldots, c) \qquad (19)$$

When $x_i$ approaches unity, $\mu_i$ approaches $\mu_i^{\circ}$, thus giving us the result that in the limit the activity coefficient $\gamma_i$ is unity. The change of the chemical potential at mixing is given by

$$\mu_i^m = \mu_i - \mu_i^{\circ} = RT \ln (x_i\gamma_i) = RT \ln a_i \quad (i = 1, 2, \ldots, c) \qquad (20)$$

where $a_i$ is defined to be the activity of component i in a non-ideal system with respect to some reference system.

The free energy of mixing of a non-ideal system of c components can be then written as

$$g^m(\text{real}) = RT \sum_{i=1}^{c} x_i \ln (x_i\gamma_i) . \qquad (21)$$

The difference between the molal thermodynamic function of mixing and the value corresponding to a perfect solution at the same temperature, pressure, and composition as the system, is called the <u>thermodynamic excess function</u>. Thus for the Gibbs free energy function we have the following relationships:

$$g^E = g^m(\text{real}) - g^m(\text{ideal}) = RT \sum_{i=1}^{c} x_i \ln \gamma_i \qquad (22)$$

The excess functions permit a direct representation of the deviations from the laws of perfect solutions. The excess function notation was first introduced by Scatchard (1).

Upon differentiating equation (22) partially with respect to the moles of any constituent i, one obtains

$$\left(\frac{\partial G^E}{\partial n_i}\right)_{T,P,n_j(j\neq i)} = RT \ln \gamma_i + RT \sum_{j=1}^{c} n_j \frac{\partial \ln \gamma_j}{\partial n_i} \qquad (23)$$

remembering that

$$G^E = g^E \sum_{i=1}^{c} n_i . \qquad (24)$$

At constant temperature and pressure, the second part of equation (23) is another form of equation (8), and thus equation (23) reduces to the following form

$$\left(\frac{\partial G^E}{\partial n_i}\right)_{T,P,n_j(j\neq i)} = RT \ln \gamma_i = \mu_i^E \quad (i = 1,2,\ldots, c) \qquad (25)$$

It should be noted that equations (4) and (7) must be identically satisfied by the experimental data and any functional form that may be used to represent the experimental data. Furthermore all the equations in the preceding section follow as a consequence of equations (4) and (7). Of pertinent value to this research is the fact that when one specifies an extensive function, such as the excess free energy, in terms of the compositions of the components of a system in mole fractions, using any functional form whatsoever, the Gibbs-Duhem equation (equation (8)) in terms of the excess chemical potentials is automatically satisfied. This is an example of an application of Euler's Theorem on homogeneous functions

(33). Equation (25) then can be considered as defining the procedure for the computation of the excess chemical potential when the functional form of the excess free energy is given. Thus one can readily see that if the original set of data are measurements of some extensive thermodynamic function, such as the heat of mixing given as some function of the mole fractions, then the computed partial quantities will always satisfy the Gibbs-Duhem equation (equation (8)). Examples of the incorrect use of these "tests" of thermodynamic consistency are pointed out in the published literature (34). The conclusion of this discussion is that in order to examine data for thermodynamic consistency, the partials of the extensive quantities must themselves be the experimentally determined quantities. This conclusion was also arrived at by van Ness (34).

Computation of the excess chemical potential function.--This section continues the discussion of fundamental thermodynamic relationships. In the previous section, some relations between the excess free energy and the excess chemical potential were developed. Equation (25) relates the excess chemical potential to both the excess free energy function and the activity coefficient. It should be noted that there are two distinct considerations involved which should be kept clearly in mind. One is the fact that a model can be postulated to represent the functional relationship between the excess chemical potentials and the liquid compositions. The parameters of any such model are determined from experimental data. The other consideration is that for each datum of the set of vapor-liquid equilibrium data, the value of the activity coefficients and hence the excess chemical potential, can be computed without the assumption of the model. This section, therefore, presents the equations which will be used for the computation of the value of the excess chemical potential from the

available experimental data. The method of the evaluation of the parameters of an assumed model for all the values of the excess chemical potentials of a vapor-liquid equilibrium experiment will be discussed below.

The starting point of this discussion will be the equations derived by Beattie (35) for the excess chemical potential.

$$\mu_i^E = RT \ln \gamma_i = RT \ln \frac{Py_i}{P_i^o x_i} + \int_0^P \left[\left(\frac{\partial v}{\partial n_i}\right)_{T,P,n_j} - \frac{RT}{P}\right] dP$$

$$- \int_0^{P_i^o} \left[\frac{v}{n_i} - \frac{RT}{P}\right] dP + \int_P^{P_i^o} v_i dP \qquad (26)$$

For the useful solution of equation (26), a volume-explicit equation of state must be assumed. It can also be shown that the excess chemical potential is related to the volumetric properties (35),

$$\mu_i^E = RT \ln \frac{PV_m}{p_i^o V_i^o x_i} + \lim_{V' \to \infty} \int_{V_m'}^{V'} \left[\left(\frac{\partial P}{\partial n_i}\right)_{V,T,n_j} - \frac{RT}{V_m}\right] dV$$

$$+ \lim_{V' \to \infty} \int_V^{V'} \left[\left(\frac{\partial P}{\partial n_i}\right)_{V,T} - \frac{RT}{V}\right] dV - \int_{P_i^o}^P v_i^o \, dP \qquad (27)$$

The evaluation of the integrals in equation (27) requires a pressure explicit form of the equation of state. Integration of equation (27) yields an equation containing expressions which involve the volume of the mixture. Traditionally, in vapor-liquid phase equilibrium computations, the use of a volume explicit equation-of-state in equation (26) has been favored over the use of a pressure explicit equation-of-state in equation (27) especially in the low pressure regions. The reason for this becomes

obvious when one considers that the raw data from a vapor-liquid equilibrium experiment consists of a total pressure and temperature measurement at some vapor and liquid composition. Hence to use a pressure explicit equation-of-state to determine the mixture volumes when all the parameters (i.e., virial coefficients) are not known to the desired degree of precision, introduces an error at least as great as the correction that one is trying to make for the vapor phase imperfections. Thus, the more direct approach would be to use the integrated form of equation (26) with a volume explicit equation-of-state.

Of the different possible equations-of-state, the following equation, which is discussed in Appendix A, is used for the binary mixture.

$$V = \frac{RT}{P} + B_{11}y_1^2 + 2B_{12}y_1y_2 + B_{22}y_2^2 \qquad (28)$$

Equation (28) is usually modified to the following form,

$$V = \frac{RT}{P} + B_{11}y_1 + B_{22}y_2 + R_{12}y_1y_2 \qquad (29)$$

where

$$R_{12} = 2B_{12} - B_{11} - B_{22} \qquad (30)$$

Substitution of equation (29) into equation (26) and performing the integration yields for a binary mixture, the following equations for each of the components:

$$\mu_1^E = RT \ln \gamma_1 = RT \ln \frac{Py_1}{P_1^o x_i} + (B_{11} - V_1^o)(P-P_1^o) + R_{12}Py_2^2 \qquad (31)$$

$$\mu_2^E = RT \ln \gamma_2 = RT \ln \frac{Py_2}{P_2^o x_2} + (B_{22} - V_2^o)(P-P_2^o) + R_{12}Py_1^2 \qquad (32)$$

Equations (31) and (32) have been used to such a great extent in vapor-liquid equilibrium calculations that, in effect, they are now standard. One should keep in mind all the assumptions used in their development (see Appendix A), and that these equations are not the most precise and, in some instances, perhaps not even the best to use. The latter case is true when the contribution by the vapor phase imperfection terms of equations (31) and (32) is of the same order of magnitude as the logarithm term. This occurs when vapor-liquid equilibrium mixtures are very nearly ideal solutions, (the excess Gibbs free energy is small). It is also true that in these cases, the virial coefficients of mixing are not always available. For solutions which deviate greatly from ideal solutions, the contribution of the vapor phase imperfection term becomes small when compared to the logarithm term.

Virial coefficient data are usually not available in the literature and some means of estimation must be employed. For all the pure substances considered in this work, experimental values of the second virial coefficients were found and are summarized in Appendix B. These virial coefficient data given as functions of temperature were correlated to the Berthelot equational form using the method of least squares. By using this basic equational form along with suitable combination rules, the second virial coefficients of the binary mixtures could be easily estimated. For mixtures of non-polar molecules and for mixtures of polar-non-polar molecules, the Lorentz-Berthelot mixture rule (36) was used for computing the second virial coefficients of binary mixtures. (See Appendix A for a complete discussion of these computations.)

The general ternary equation.--In the preceding section, the equations for the computation of the values of the excess chemical potentials were discussed. This section presents only those postulated models for the excess free energy which will be used in this thesis. Wohl (3) has proposed the following equation as a general expression for the excess free energy in terms of the liquid phase compositions

$$g^E/2.3RT = \Sigma\, q_i x_i \left(\sum_{ij} z_i z_j a_{ij} + \sum_{ijk} z_i z_j z_k a_{ijk} + \sum_{ijkl} z_i z_j z_k a_{ijkl} + \cdots\right) \qquad (33)$$

In this expression $g^E = G^E/n$ is the molar excess free energy, and $q_i$, $q_j$, $q_k$, and $q_l$ are parameters which Wohl has called the effective molar volumes of the components i, j, k, and l. The quantities $z_i$, $z_j$, $z_k$, and $z_l$ are the effective volumetric fractions of these components and are defined by

$$z_i = q_i x_i / \sum_j q_j x_j \qquad (34)$$

and satisfy the condition

$$\sum_i z_i = 1 \qquad (35)$$

The empirical constants, $a_{ij}$, $a_{ijk}$, and $a_{ijkl}$ are said to be related to the interactions in the various groups of molecules ij, ijk, and ijkl.

The first summation ( $\sum_{ij}$ ) in equation (33) gives the sum of the products of the volumetric fractions $z_i$, $z_j$ of all pairs of dissimilar constituents that can be chosen from a given n-component system, and

where each product is multiplied by a constant $a_{ij}$ which is related to the force interactions between corresponding pairs of molecules.

Similarly the second summation ( $\sum_{ijk}$ ) gives the sum of the products of the volumetric fractions, $z_i$, $z_j$, $z_k$ of all triplets of at least partially dissimilar constituents that can be chosen from the given n-component system, where each product is multiplied by a constant $a_{ijk}$, which is said to be related to the force interaction among the triplets of molecules. It should be noted that in equation (33) in all cases terms for which the subscripts are equal (i.e., i = j = k = ... ) are to be excluded from the sums.

Following the development given by Wohl, the first three summations of equation (33) were taken and expanded. The terms were rearranged and the parameters, $a_{ij}$, $a_{ijk}$, and $a_{ijkl}$ were combined into twelve parameters plus the three q-parameters ($q_1$, $q_2$, and $q_3$) to give the following equation for the excess free energy of a ternary mixture:

$$\begin{aligned} g^E/2.3RT = & \left[(q_1x_1 + q_2x_2 + q_3x_3)/q_1\right] \; z_1z_2(A_{21}z_1q_1/q_2 + \\ & A_{12}z_2 - D_{12}z_1z_2) + z_1z_3(A_{31}z_1q_1/q_3 + A_{13}z_3 - \\ & D_{13}q_1z_1z_3/q_3) + z_2z_3(A_{32}z_2q_1/q_3 + A_{23}z_3q_1/q_2 - \\ & D_{23}z_2z_3q_1/q_2) + z_1z_2z_3(A_{21}q_1/q_2 + A_{13} + \\ & A_{32}q_1/q_3 - z_1c_1 - z_2c_2q_1/q_2 - z_3c_3q_1/q_3) \end{aligned} \qquad (36)$$

By use of equation (25) and equation (36), the equations for the activity coefficients of each component are obtained. The relationship of the activity coefficients to excess chemical potentials is given by equation (25). The ternary activity coefficients in terms of liquid compositions and

undetermined parameters are given in the following equations which are used in this thesis:

$$\log \gamma_1 = z_2^2(1 - 2z_1)A_{12} - 2z_2z_3^2 (q_1/q_2) A_{23} + 2z_1z_3 (z_2 + z_3) A_{31} + z_2(2z_1z_2 + z_3)(q_1/q_2)A_{21} + z_2z_3 (2z_3 - 1)(q_1/q_3)A_{32} + z_3(z_2 + z_3)(1 - 2z_1)A_{13} + z_1z_2^2(3z_1 - 2)D_{12} + 3z_2^2z_3^2(q_1/q_2)D_{23} + z_1z_3^2(3z_1 - 2)(q_1/q_2)(q_1/q_2)D_{13} - z_1z_2z_3(2 - 3z_1)C_1 - z_2^2z_3 (1 - 3z_1)(q_1/q_2)C_2 - z_2z_3^2(1 - 3z_1(q_1/q_3)C_3 \quad (37)$$

$$\log \gamma_2 = 2z_1z_2(z_1 + z_3)A_{12} + z_3^2(1 - 2z_2)A_{23} - (q_2/q_3) A_{31} + z_1(z_1 + z_3)(1 - 2z_2) A_{21} + z_3 (2z_2z_3 + z_1)(q_2/q_3)A_{23} + z_1z_3(2z_1 - 1)(q_2/q_3)A_{13} + z_2z_1^2(3z_2 - 2)(q_2/q_3)D_{12} + z_2z_3^2(3z_2 - 2)D_{23} + 3z_1^2z_3^2(q_2/q_3)D_{13} + -z_3z_1^2(1 - 3z_1)(q_2/q_1)C_1 - z_1z_2z_3(2 - 3z_2)C_2 - z_3^2z_1(1 - 3z_2)q_2/q_3 C_3 \quad (38)$$

$$\log \gamma_3 = 2z_1z_2^2(q_3/q_1)A_{12} + 2z_2z_3(z_2 + z_1) A_{23} + z_1^2(1 - 2z_3)A_{31} + z_1z_2(2z_2 - 1)(q_3/q_2)A_{21} + z_2 (z_1 + z_2)(1 - 2z_3)A_{32} + z_1(2z_1z_3 + z_2)(q_3/q_1)A_{23} + 3z_1^2z_2^2(q_3/q_1) D_{12} + z_3z_2(3z_3 - 2)(q_3/q_1) D_{23} + z_3z_1^2(3z_3 - 2) D_{13} - z_1^2z_2(1 - 3z_3) q_3/q_1 C_1 - z_1z_2^2(1 - 3z_2)(q_3/q_2)C_2 - z_1z_2z_3(2 - 3z_3)C_3 \quad (39)$$

Computation of the parameters of specific models.--In the previous sections the equations for the computations of the excess free energy of a ternary mixture and the excess chemical potentials of binary mixtures were presented. Equation (36) for the computation of the excess free energy of a ternary mixture is empirical in nature with twelve parameters to be determined. By the use of equation (25), equations can be obtained for the activity coefficients of each of the components of a ternary mixture (equations (37), (38), and (39)). By specifying certain relationships for three of these parameters, $q_1$, $q_2$, and $q_3$, the relationship of the ternary equations to certain forms of the binary equations can easily be shown. In this section the binary equations which are used in this thesis are presented, and some of the methods used in the computation of the parameters of these equations are discussed. The data required for these computations are the activity coefficients for each binary component as a function of the liquid composition. These values can be obtained from experimental vapor-liquid equilibrium data with the aid of equations (31) and (32). The following discussion will be given for a binary system consisting of components one and two. It is understood that this discussion can be extended to the other binary pairs of a ternary system with no difficulty. It should also be noted that the following discussion is not new in that much of it can be found in Wohl's paper (3), but it is presented here for the sake of clarifying the discussions in the succeeding chapters of this thesis.

The general binary equations are derived from equations (37) and (38), for the binary system consisting of components one and two, by letting $z_3 = 0$. The resulting equations are usually called the binary q-equations and are given as follows:

$$\log \gamma_1 = z_2^2(1 - 2z_1)A_{12} + 2z_1z_2^2(q_1/q_2)A_{21} + z_1z_2^2(3z_1 - 2)D_{12} \quad (40)$$

$$\log \gamma_2 = 2z_1^2z_2(q_1/q_2)A_{12} + z_1^2(1 - 2z_2)A_{21} + z_1^2z_2(3z_2 - 2)(q_1/q_2)D_{12} \quad (41)$$

where

$$z_1 = x_1/(x_1 + x_2(q_2/q_1)) \text{ and } z_2 = 1 - z. \quad (42)$$

If the ratio, $q_1/q_2$, is set equal to one, then equations (40) and (41) become the Margules three-constant equations.

$$\log \gamma_1 = x_2^2(1 - 2x_1)A_{12} + 2x_1x_2^2A_{21} + x_1x_2^2(3x_1 - 2)D_{12} \quad (43)$$

$$\log \gamma_2 = 2x_1^2x_2A_{12} + x_1^2(1 - 2x_2)A_{21} + x_1^2x_2(3x_2 - 2)D_{12} \quad (44)$$

When the constant $D_{12}$ is set equal to zero, equations (43) and (44) reduce to the Margules two-constant equations.

$$\log \gamma_1 = x_2^2(1 - 2x_1)A_{12} + 2x_1x_2^2A_{21} \quad (45)$$

$$\log \gamma_2 = 2x_1^2x_2A_{12} + x_1^2(1 - 2x_2)A_{21} \quad (46)$$

When the ratio $(q_2/q_1)$ is set equal to the ratio of the molal volumes $(v_2/v_1)$ in equations (40) and (41), the Scatchard-Hamer three-constant equations are obtained.

$$\log \gamma_1 = z_2^2(1 - 2z_1)A_{12} + 2z_1z_2^2(v_1/v_2)A_{21} + z_1z_2^2(3z_1 - 2)D_{12} \quad (47)$$

$$\log \gamma_2 = 2z_1^2z_2(v_2/v_1)A_{12} + z_1^2(1 - 2z_2)A_{21} + z_1^2z_2(3z_2 - 2)(v_2/v_1)D_{12} \quad (48)$$

where $$z_1 = x_1v_1/(x_1v_1 + x_2v_2) \text{ and } z_2 = 1 - z_1 . \quad (49)$$

If the parameter $D_{12}$ is set equal to zero, the Scatchard-Hamer-two-constant equations are obtained.

$$\log \gamma_1 = z_2^2(1 - 2z_1)A_{12} + 2z_1z_2^2(v_1/v_2)A_{21} \qquad (50)$$

$$\log \gamma_2 = 2z_1^2z_2(v_2/v_1)A_{12} + z_1^2(1 - 2z_2)A_{21} \qquad (51)$$

When the ratio $q_1/q_2$ is set equal to $A_{12}/A_{21}$ in equations (40) and (41), van Laar three-constant equations are obtained.

$$\log \gamma_1 = z_2^2A_{12} + z_1z_2^2(3z_1 - 2)D_{12} \qquad (52)$$

$$\log \gamma_2 = z_1^2A_{21} + z_1^2z_2(3z_2 - 2)(A_{21}/A_{12})D_{12} \qquad (53)$$

where $$z_1 = x_1/(x_1 + x_2(A_{21}/A_{12})) \text{ and } z_2 = 1-z_1 \qquad (54)$$

When the constant $D_{12}$ is set equal to zero, the van Laar two-constant equations are obtained.

$$\log \gamma_1 = z_2^2A_{12} = A_{12}/1 + (x_1A_{12}/x_2A_{21})^2 \qquad (55)$$

$$\log \gamma_2 = z_1^2z_{21} = A_{21}/1 + (x_2A_{21}/x_1A_{12})^2 \qquad (56)$$

The Margules equations (equations (43) through (46) and the Scatchard-Hamer equations (equations (47), (48), (50), and (51)) are linear in the parameters, $A_{12}$, $A_{21}$, and $D_{12}$ and thus can be evaluated by the method of least squares. It was observed by the author that the equations for the ratio of the activity coefficients used for the evaluation of the parameters gave a better fit to the experimental data than taking each of the above-mentioned equations separately. Thus for the evaluation of the parameters (or constants) of the Margules three-constant activity

coefficient equations, the following equation would be used,

$$\log (\gamma_1/\gamma_2) = x_2(1 - 3x_1)A_{12} + x_1(2 - 3x_2)A_{21} + x_1x_2(4x_1 - 2)D_{12} \qquad (57)$$

For the determination of the parameters of the Margules two-constant equations, only the first two terms of equation (57) would be used in the least squares fit of the data (equation (58)).

$$\log (\gamma_1/\gamma_2) = x_2(1 - 3x_1)A_{12} + x_1(2 - 3x_2)A_{21} \qquad (58)$$

In a like manner the constants to the Scatchard-Hamer equations would be evaluated by the following equation,

$$\begin{aligned} \log (\gamma_1/\gamma_2) = {} & z_2(2z_1^2(1 - v_2/v_1) + (1 - 3z_1))A_{12} \\ & (z_1/v_2)(2z_1^2(v_1 - v_2) + z_2(v_2 - 4v_1) + 2v_1)A_{21} + \\ & (z_1z_2/v_1)(3z_1^2(v_1 - v_2) + z_1(5v_2 - v_1) - 2v_2)D_{12} \end{aligned} \qquad (59)$$

Also the evaluation of constants for the two-constant Scatchard-Hamer equations involve the use of equation (59) with the last term removed from the right side (equation (60)).

$$\begin{aligned} \log(\gamma_1/\gamma_2) = {} & z_2(2z_1^2(1 - v_2/v_1) + (1 - 3z_1))A_{12} + \\ & (z_1/v_2)(2z_1^2(v_1 - v_2) + z_2(v_2 - 4v_1) + 2v_1)A_{21} \end{aligned} \qquad (60)$$

The constants, $A_{12}$, $A_{21}$, and $D_{12}$ are not linear in the van Laar equations (equations (52), (53), (55), and (56)) and therefore they can not be determined by the simple least squares procedure used for the Margules and Scatchard-Hamer equations. In fact, there is no convenient

method of evaluating the parameter, $D_{12}$, from the experimental data in equations (52) and (53) and therefore these equations will not be considered any further. It is possible, however, to use a least squares procedure to evaluate the constants, $A_{12}$ and $A_{21}$, if equations (55) and (56) are rewritten in the following form,

$$(\log \gamma_1)^{-0.5} = (x_1/x_2)\sqrt{A_{12}} / A_{21} + 1/\sqrt{A_{12}} \qquad (61)$$

$$(\log \gamma_2)^{-0.5} = (x_2/x_1)\sqrt{A_{21}} / A_{12} + 1/\sqrt{A_{21}} \qquad (62)$$

The method of evaluating these constants will be discussed in the next chapter.

# CHAPTER III

## PROCEDURE FOR PREDICTING TERNARY LIQUID-LIQUID EQUILIBRIUM

This chapter contains a description of the procedure by which the ternary liquid-liquid equilibria (i.e., binodal curve with tie-lines) were computed from binary equilibrium data. The basis for all the computations was the Wohl equation for the excess free energy (equation (36)). By specifying relationships to the three parameters, $q_1, q_2$, and $q_3$, Wohl showed that this general equation can be transformed to equations proposed by van Laar, Margules, and Scatchard and Hamer (3). It is these latter equations which will be used for the ternary computations. These equations taken collectively are referred to as the standard binary activity coefficient equations. Specifically, they consist of the following named equations:

(a) two-constant Margules (equations (45) and (46))

(b) three-constant Margules (equations (43) and (44))

(c) two-constant van Laar (equations (55) and (56))

(d) two-constant Scatchard-Hamer (equations (50) and (51))

(e) three-constant Scatchard-Hamer (equations (47) and (48))

The first objective of this procedure is to obtain the best values for the constants of the standard binary activity coefficient equations. It should be noted that, in general, some equational form (or model) is postulated for the excess free energy instead of the activity coefficients

in terms of liquid molal compositions and empirical coefficients for both binary and ternary systems. Partial differentiation with respect to each of the mole numbers yields equations of the logarithms of the activity coefficients as functions of the liquid compositions and the same coefficients. The values of the coefficients of these equations can be computed from the experimental data in either the excess free energy function or the derived activity coefficient functions. The data are fitted to the activity coefficient functions in lieu of the excess free energy functions. This choice was dictated by a desire to examine the experimental vapor-liquid equilibrium data for thermodynamic consistency.

Figure 1 shows the relationships and the various flows of information in this research.

The collection of data from the literature.--A literature survey was made to collect most of the data used in this research. The following data at the same constant temperature were sought:

(a) Vapor-liquid equilibrium data for a partially miscible ternary system.

(b) Liquid-liquid equilibrium data for the same ternary system.

(c) Vapor-liquid equilibrium data for all the component binary systems.

(d) Liquid-liquid equilibrium data for all the component binary systems.

The values obtained from the ternary experimental data could be checked against values predicted from the binary data. These particular data would also test the assumption that the ternary constants were negligible. This is the assumption which is implied in the computation of ternary equilibrium data using binary equilibrium data only.

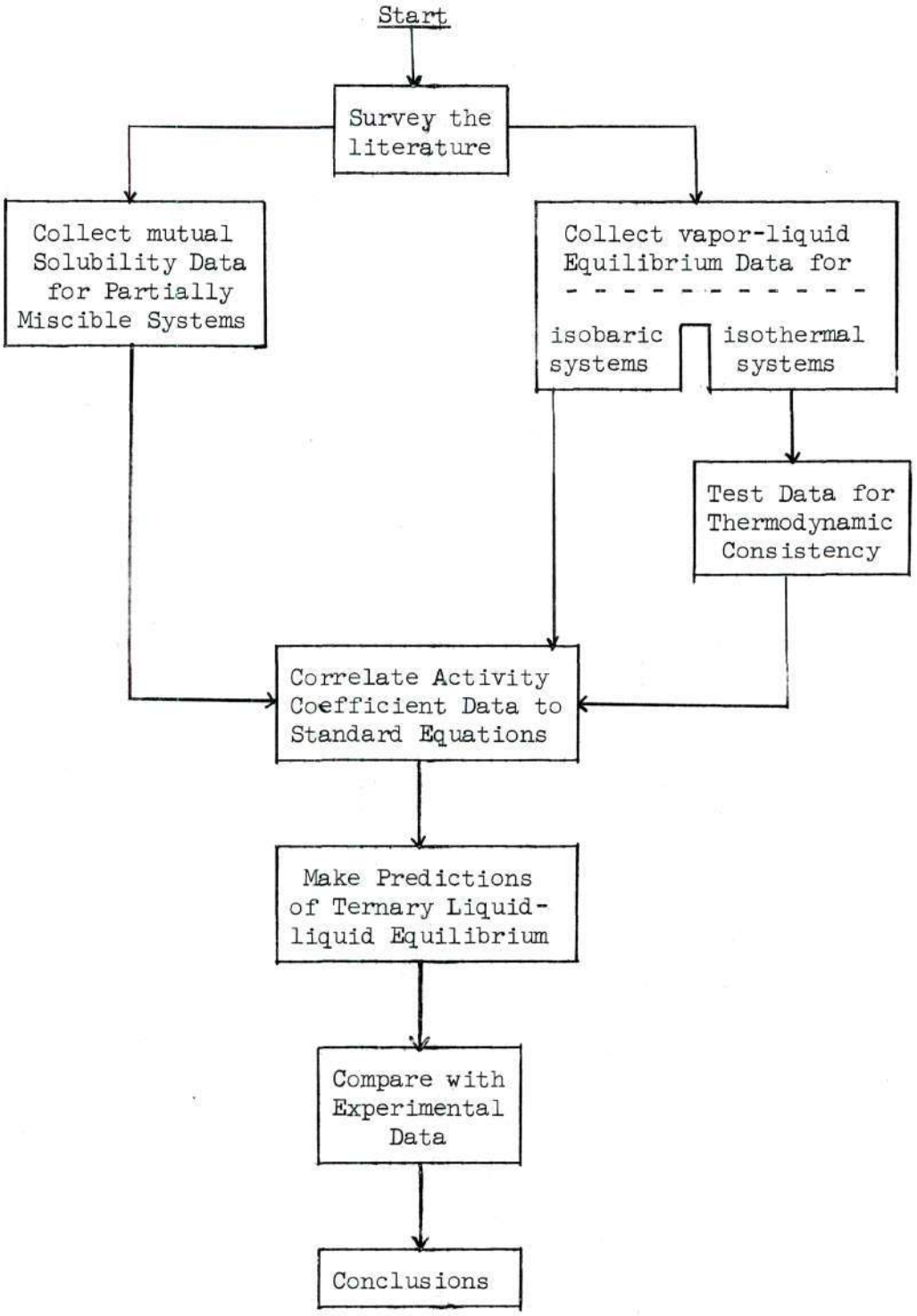


Figure 1. A Flow Diagram of the Procedure Used in this Thesis.

The above listed collective set of data was not found in the published literature. In fact, no isothermal vapor-liquid equilibrium data for a partially miscible ternary system were found. There were only five partially miscible ternary systems for which isobaric vapor-liquid equilibrium data were found in the literature. All but two of the above isobaric ternary equilibrium data were discarded because data for the component binary systems could not be found.

The procedure for the literature search, therefore, became one of surveying the published literature for available isothermal binary vapor-liquid equilibrium data, and then matching up these sets to available ternary liquid-liquid equilibrium data. The following major secondary sources of published data were used in the literature search:

(a) Chemical Abstracts, 1947-1959.

(b) Chu, J. C., Getty, R. J., Brennecke, L. F., and Rajendra, P., Distillation Equilibrium Data, Reinhold Publishing Corporation, New York (1950).

(c) Chu, J. C., Wang, S. L., Levy, S. L., and Paul, R., Vapor-liquid Equilibrium Data, J. W. Edwards, Publishers, Inc., Ann Arbor, Michigan (1956).

(d) Hala, E., Pick, J., Fried, V., and Vilim, O., Vapor-Liquid Equilibrium, Pergamon Press, New York (1958).

(e) Timmermans, J., The Physico-Chemical Constants of Binary Systems in Concentrated Solutions, Vols. I and II, Interscience Publishers, Inc., New York, (1959).

(f) Himmelblau, D. M., Brady, B. L., and McKetta, J. J., Survey of Solubility Diagrams for Ternary and Quaternary Liquid Systems, Special Publication No. 30, Bureau of Engineering Research, The University of Texas, Austin, Texas, (1959).

These secondary sources provided references to the original papers which were examined for possible use. The systems were selected without a priori

knowledge of the validity of the published data. Table 1 summarizes the binary systems which were selected on the basis of the availability of the vapor-liquid equilibrium data and the ability to be matched to published ternary liquid-liquid equilibrium data.

It must be pointed out that for partially miscible and immiscible binary systems, the virtual absence of vapor-liquid equilibrium data necessitated that liquid-liquid temperature-composition data be used. Table 2 summarizes the partially miscible and immiscible binary systems used in this study.

Table 1. A Summary of the Miscible Binary Systems Used in this Study

| | |
|---|---|
| Water - acetone | Benzene - n-heptane |
| Water - pyridine | Benzene - nitromethane |
| Chloroform - acetone | Benzene - pyridine |
| Benzene - ethanol | n-Octane - isooctane |
| Water - ethanol | n-Heptane - cyclohexane |

Table 2. A Summary of the Partially Miscible and Immiscible Binary Systems used in this Study.

| | |
|---|---|
| Furfural - n-heptane | Nitromethane - n-heptane |
| Furfural - cyclohexane | Nitroethane - n-octane |
| Aniline - n-heptane | Nitroethane - isooctane |
| Aniline - cyclohexane | Benzene - water |
| | Chloroform - water |

The Treatment of Binary Vapor-Liquid Equilibrium Data

This section develops the procedure by which the collected binary equilibrium data are treated. The objective in this section on the treatment of binary systems is to use the available information to obtain values of the parameters in the standard binary activity coefficient equations. This process may also be described as one of correlating the data by each of the standard binary equations which were discussed at the beginning of this chapter. The binary systems are considered as being in one of three possible categories which are summarized as:

(1) ideal systems

(2) non-ideal miscible systems

(3) partially miscible or immiscible systems

A binary system is considered to be ideal if the excess free energy of the mixture is either zero or very small. For these systems the parameters of the standard binary equations are zero. In this study a system was classified as an ideal system either by assumption, or if the available experimental data indicated a small excess free energy for the binary system. The basis for assuming a system to be ideal was that experimental data were not available and that the mixture consisted of similar compounds.

Binary systems which form two liquid phases upon mixing of the binary constituents are classified as partially miscible or immiscible systems depending upon the extent of the mutual solubility. Since vapor-liquid equilibrium data were not available for most of these systems, the following procedure was employed. One of the two-suffix equations was presumed to be valid (i.e., to satisfactorily describe the activity

coefficients in the homogeneous regions), and the parameters were computed for that equation from the mutual solubility data by methods outlined in Treybal (39). The only means of checking the validity of the assumption of the applicability of any of the standard binary equations is to use vapor-liquid equilibrium data for that particular binary system.

If a partially miscible binary system had vapor-liquid equilibrium data available at temperatures above its upper critical solution temperature, then the interesting possibility exists of checking an assumed model. For, if one computes the correlation parameters of an assumed model from the mutual solubility data at temperatures below the critical solution temperature, then an approximately linear relationship often exists between these correlation parameters and the reciprocal of the absolute temperatures (40). Thus values of the parameters can be extrapolated to temperatures above the critical solution temperature, if the curvature is not too great, and a check can be made with the same assumed model for the vapor-liquid equilibrium data.

The published data for the non-ideal miscible systems consisted of either isobaric or isothermal vapor-liquid equilibrium studies. The procedure for the treatment of the isobaric data will be discussed first, followed by a discussion of the treatment of isothermal data.

Isobaric equilibrium data were used when they were the only data available for a particular component binary system of a ternary system. The published experimental data were used to compute the values of the activity coefficients by equations (31) and (32) except that no corrections were made for gas phase imperfections. The activity coefficients so obtained were used as ratios, as given in equations (57) through (60), to obtain the parameters of the Margules and Sctachard-Hamer equations by the

method of least squares. Another technique, which was investigated for only two systems, was to compute the values of the parameters to the Margules and Scatchard-Hamer equations explicit in the activity coefficients of each component by the method of least squares. Thus three sets of parameters were obtained for each of the Margules and Scatchard-Hamer equations (viz., equations (43) to (51)). On the basis of the studies on the two systems considered (nitromethane--benzene, and benzene--n-heptane), it was concluded that the best parameters to the Margules and Scatchard-Hamer equations were obtained by a least squares fit of the ratio of the activity coefficients in terms of the liquid compositions. Thus the constants for the two-constant Margules equations (equations (45) and (46)) were obtained from a fit of the experimental data by equation (58). The constants for the three-constant Margules equations (equations (43) and (44)) were obtained from a fit of the data by equation (57). The constants for the two-constant Scatchard-Hamer equations (equations (50) and (51)) were obtained from a fit of the data by equation (60). The constants for the three-constant Scatchard-Hamer equations (equations (47) and (48)) were obtained from a fit of the data by equation (59). The constants for the two-constant van Laar equations (equations (55) and (56)) were obtained by a least squares fit of the data by a slightly different procedure, which is discussed at the end of this section.

Thus after having obtained the parameters to all of the standard binary activity coefficient equations, it was desired to know which one

pair out of this set of binary equations best represented the data. The criterion used was that the best fitting pair of equations out of all of the standard binary equations had the smallest value of the sums of squares of residuals for activity coefficients one and two.

The relationship of the values of the parameters determined from isobaric data to be used in isothermal computations is not always clear. If the temperature difference between the maximum and the minimum temperatures which an isobaric equilibrium system can have, is a small number, the system is usually considered to be essentially an isothermal system. If the temperature difference is large, one usually assumes that the correlation parameters do not vary greatly with temperature anyway, and proceeds to use them in an isothermal sense. If the isobaric data are the only available data then one has no recourse but to make either of the above two assumptions and proceed with the computations.

The values of the coefficients for each of the standard binary equations are found in Appendix D along with values of the sums of squares of residuals for the fit of each of the equations to the ratio of the activity coefficients and to the activity coefficients of each component. This least squares fitting procedure was programmed for the Burroughs 220 computer located at the Rich Electronic Computer Center at Georgia Institute of Technology, Atlanta, Georgia.

The activity coefficients for the non-ideal miscible binary systems were computed by equations (31) and (32). These activity coefficients were fitted to the standard binary equations using the same least squares procedure as that described for the isobaric system, except that gas phase imperfections were taken into account. The basic experimental data of

total pressure, vapor and liquid compositions for some of the binary systems (namely, water-acetone, water-pyridine, benzene-ethanol) were tested for thermodynamic consistency by the methods outlined in Part II of this thesis. One of the computed quantities of the consistency test is a set of values of the activity coefficients, computed by equations (31) and (32), for ninety-nine values of the liquid compositions. These activity coefficients were computed from a fit of the experimental data, while the previously discussed activity coefficients were computed from the experimental data themselves. This set of ninety-nine activity coefficients were then fitted to the standard binary equations in the manner described for the isobaric systems. It was observed that the parameters obtained from either set did not vary appreciably from each other.

The evaluation of the constants $A_{12}$ and $A_{21}$ for the van Laar equations presents some difficulties which are not encountered in the least squares procedure for the Margules and Scatchard-Hamer equations. Therefore the next section discusses the procedure which is used only for the evaluation of the parameters of equations (55) and (56). Equations (61) and (62) are linear in the constants) ( $\sqrt{A_{12}}/A_{21}$ , $1/\sqrt{A_{12}}$ , etc.) and thus can be determined using the method of least squares. A graphical method has been demonstrated (37). One of the minor objectives of this thesis is to study the feasibility of automating this graphical procedure. The following is a discussion of the problems encountered in this particular instance.

If the data are interpreted as the ratio of the mol fractions to be functions of the reciprocal square root of the activity coefficients, the relationship should be linear if the data can be correlated by the

van Laar two-constant equations. The slopes of the straight lines are given by $\sqrt{A_{12}}/A_{21}$ and $\sqrt{A_{21}}/A_{12}$, and the intercepts are given by $1/\sqrt{A_{12}}$ and $1/\sqrt{A_{21}}$ for the composition dependence of the reciprocal square roots of log $\gamma_1$ and log $\gamma_2$ respectively. This method cannot be used for mixtures which show a negative deviation from Raoult's law as the activity coefficients are less than unity.

In most cases the data will not plot as a straight line and the problem is one of finding the "best" straight line through the given points. In this study, the term, "best" straight line is taken to be that line which gives constants for the van Laar equations such that the deviation of the computed curve of activity coefficients versus liquid composition from the experimentally determined points is a minimum. A method of finding the best straight line is one where the sums of the squares of the residuals is a minimum. A residual is a term used in this study to mean the difference between the computed value and the observed value of the activity coefficient for some particular liquid composition. Several factors must be taken into account in the application of the least squares procedure. For precise calculations, it is necessary to consider that the various measurements have different statistical weights which are functions of the errors of measurements. The assignment of a correct weighting factor to a least squares fit is a problem related directly to each individual experiment. Usually these data are not available in the literature except for the general statement that measurements of a component present in small quantities (dilute region) are more uncertain than measurements in a more concentrated region.

The second factor to be taken into account is that from the nature of the various functions, the following relations must hold,

$$\lim_{x_1 \to 0} \log \gamma_1 = A_{12} \tag{63}$$

$$\lim_{x_1 \to 1} \log \gamma_2 = A_{21} \tag{64}$$

Thus the constants in theory could be easily determined from an extrapolation of the given data plotted as a composition dependence of the logarithm of the activity coefficients; but it is precisely in this dilute region where the uncertainty of the experimental data is the greatest.

Examination of the nature of this method of correlation of the data to the van Laar equations discloses some difficulties. From a table of x versus $(x/1 - x)$, it is observed that the majority of the data (i.e., $0 < x < 0.8$) can be represented by the ratios $0 < (x/1 - x) < 4.0$. The representation of the data for equation (61) is shown in Figure 2 with the least squares fit through all the data points given by the curve marked I. The system is ethanol-benzene at 45° C (38). While the straight line (I) represents the best fit of the data in the least squares sense, the constants that were determined are very inadequate, as seen in Figure 3. From an examination of the data points, it is obvious that the data should not correlate well with the van Laar equations. We are, however, looking for the best van Laar correlation and use of all the data is certainly unsatisfactory.

If the problem were to be solved manually, in lieu of a computer, the line marked with a II would more likely be chosen, since it tends to

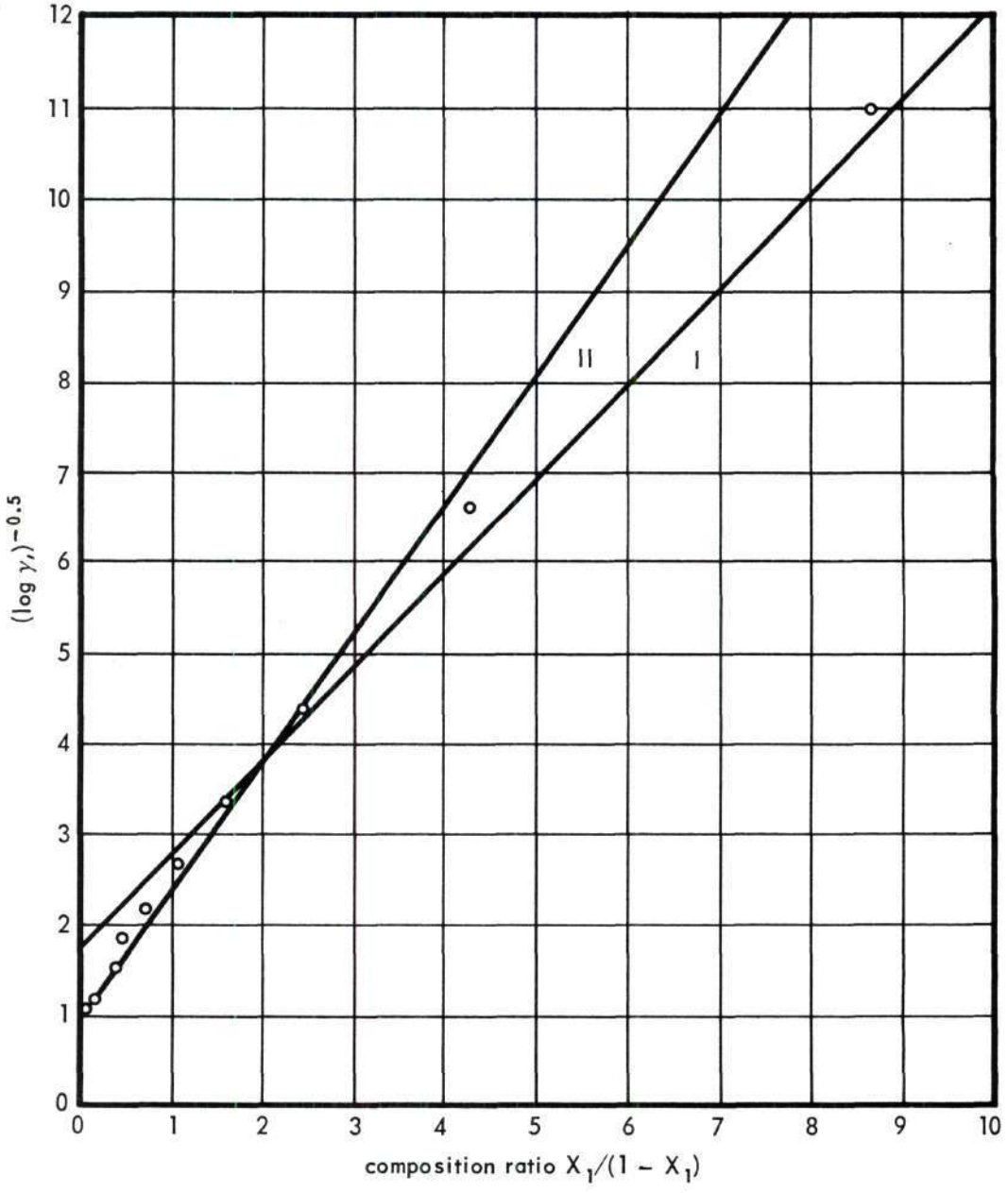


Figure 2. Least squares fit of experimental data for ethanol-benzene at 45°C. Curve I has a weighting factor of one for all data points. Curve II has a weighting factor of one for $0 < X_1/(1-X_1) < 4.0$.

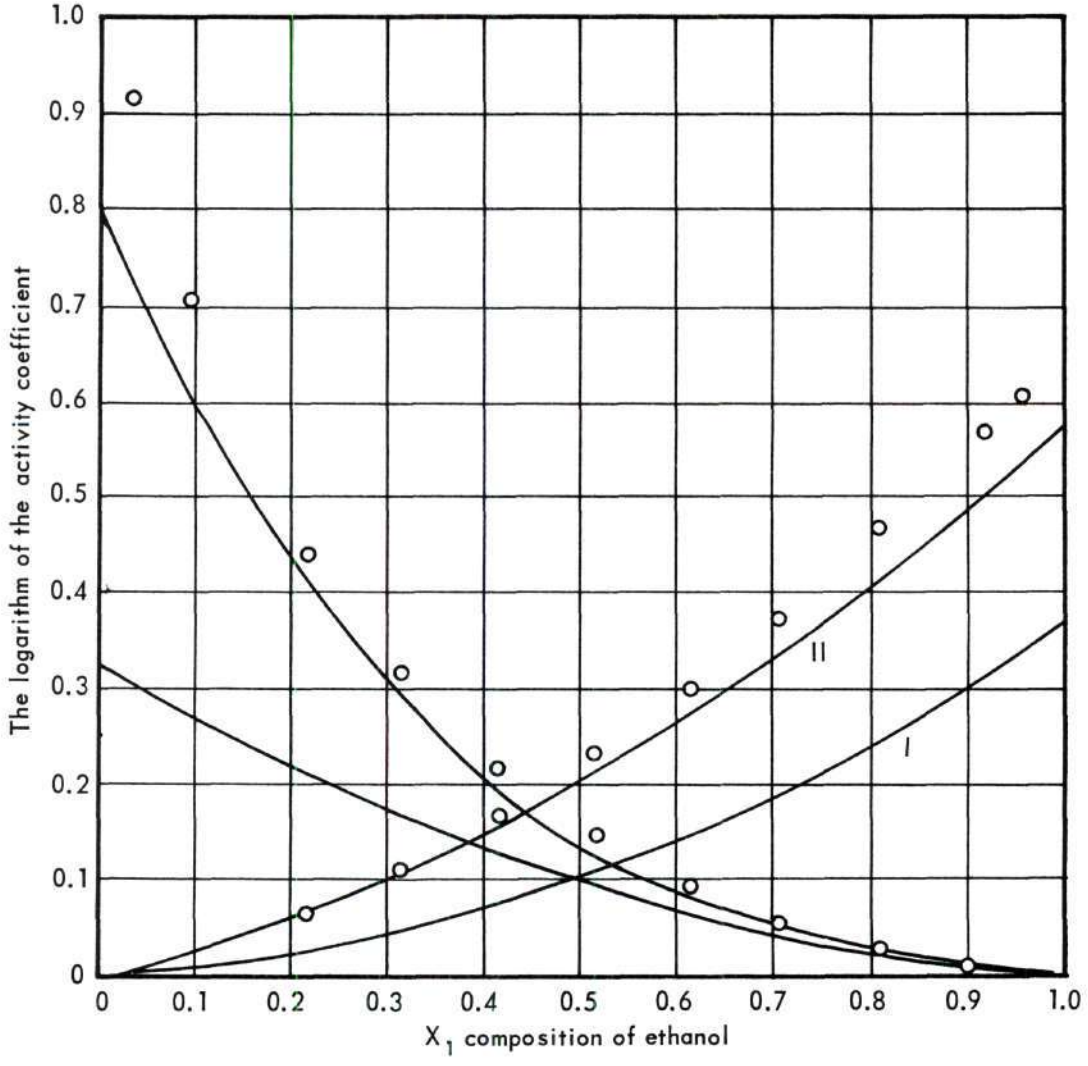


Figure 3. Computed activity coefficients for the system, ethanol-benzene at 45°C. using the least squares approximation curves I and II to the van Laar equations given in figure 1.

satisfy equations (63) and (64). To achieve this end with a computer, the solution of the problem requires a certain weighting to be introduced. Since most of the data, as pointed out above, lies in a region defined by $0 < (x/1 - x) < 4$, it was arbitrarily decided to assign points in this region a weighting factor of 1.0 and all others (i.e., for $x/(1 - x) > 4.0$) a weighting factor of zero. The results of this procedure certainly brings the correlation closer to the experimental data, although as can be seen from Figure 3 the fit is still poor. This is due to the fact that these data just do not correlate well with the van Laar equations. The precedence for this technique of correlation has been implied in the literature (37).

The parameters for the standard binary equations, obtained for the component binary systems, were then used in equations (37), (38), and (39) to compute the activity coefficients of each component of a ternary mixture. The following discussion will describe the procedure used in the prediction of the ternary liquid equilibrium.

The prediction of ternary liquid-liquid equilibrium.--The procedure used in the prediction of ternary liquid-liquid equilibrium is based upon the fact that at equilibrium the chemical potential of each component is the same in every phase (equation (11)). If a standard state of the temperature and pressure of the system is chosen, then from equations (19) and (20) it is seen that the activity of each component is the same in every phase. Hence if a function is postulated for the activity coefficients of each component in terms of liquid compositions, the activities of each component can be computed for any composition. Then, for a ternary liquid system, those compositions where the activities of each component are the

same, two liquid phases in equilibrium are indicated. The problem is to determine if there exists distinct compositions in a ternary system for which the activities of each component are the same.

The ternary system activity coefficients in this thesis are computed by equation (37), (38), and (39) with appropriate ratios of the parameters, $q_1$, $q_2$, $q_3$, determining which equation form is to be used. For example, if all the ratios of the q's were set equal to unity, then the ternary equations represent an extension of the binary Margules equations to ternary systems. Using the constants for the various binary systems of the specific models (i.e., the standard equations) the activity coefficients and then the activities of each component were computed for specific ternary compositions.

The determination of the ternary liquid-liquid equilibrium involved the following steps:

1. From a knowledge of the binary mutual solubility data, a trapezoidal region in the ternary field was arbitrarily specified for one of the phases. Subsequent discussions of ternary compositions and ternary fields will be with respect to a triangular coordinate system. This is illustrated in Figure 4.

2. The activities of each component were then computed in this region at specified intervals of composition and stored in a tabular format.

3. Values of the activities of each component were then computed for some ternary composition in the region of the other phase, which was approximately determined from the mutual solubility data of the partially miscible binary system. For example, if the ternary system consists of

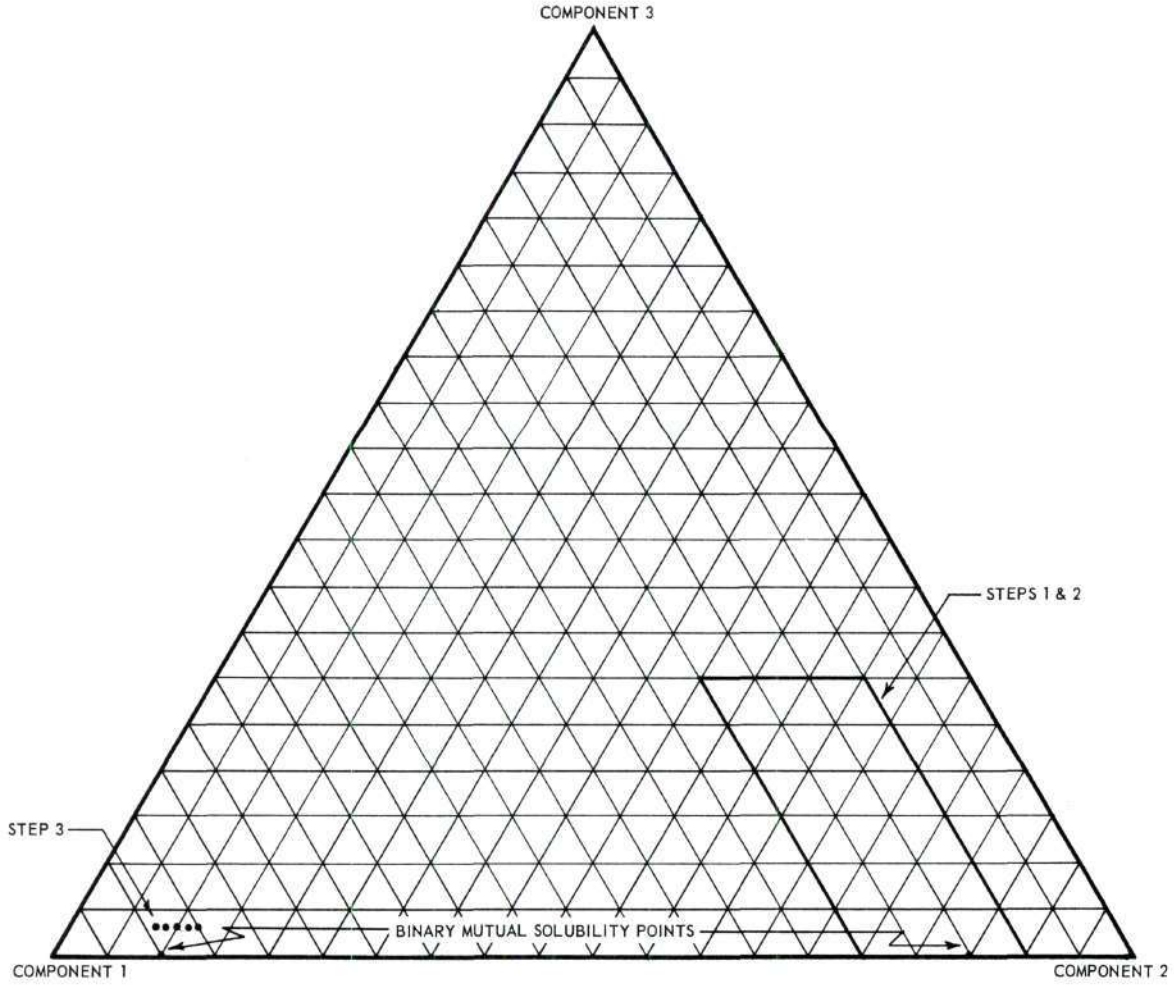


Figure 4. Illustration of the steps involved in the procedure used in the prediction of ternary liquid-liquid equilibrium.

components one, two, and three, and components one and two form a partially miscible binary system, then the trapezoidal region (described in step 1 above) might consist of composition points rich in component two. The other phase would then be in the region of composition points rich in component one. This is illustrated in Figure 4.

4. A table scanning procedure was then used to find the values of the activities of each component to be approximately the same in each phase. Specifically a quantity D, defined by equation (65) was computed.

$$D = (a_{11} - a_{12})^2 + (a_{21} - a_{22})^2 + (a_{31} - a_{32})^2 \qquad (65)$$

In equation (65) the terms $a_{ij}$ denotes the activity of component i in a j-rich liquid mixture of the ternary system. The choice of the size of the value of D was used to regulate the number of decimal places to which the activities of each component had to agree. For example, if it were specified that the differences of the activities of each component must be less than 0.001, then the maximum permissible D to satisfy this criterion would be $1.0 \times 10^{-6}$. Any values of D computed by equation (65) which were greater than this specified value of D were discarded. In practical computations the coarseness (the relatively large distance between adjacent ternary composition points) of the selected points in the trapezoidal region necessitated that D have a value of $1.0 \times 10^{-4}$ to find the values of the tie-lines.

The entire computational process was programmed for the Burroughs 220 computer with the table stored in the computer. The trapezoidal region consisted of approximately one-thousand composition points. The average distance between points was 0.01 in mole fraction compositions.

The computations for each ternary system, consisting of finding about five tie-lines, averaged about two hours of computer time.

The predicted results were then compared with the experimental ternary data in two ways. First the slopes of the predicted tie-lines were compared with the published data, and secondly, the compositions of the binodal curve were compared with the experimental values.

# CHAPTER IV

## DISCUSSION OF THE RESULTS OF TERNARY PREDICTIONS

In this chapter the results of the prediction of the ternary liquid-liquid equilibria, using the procedure outlined in the previous chapter, are presented in a summary form. The results are given for one ternary system at a time. For each system the presentation consists of the following material:

1. A summary paragraph containing some of the conclusions about the prediction method for that particular ternary system.
2. A table of the experimental liquid-liquid equilibrium data given in molal compositions. Most of the data presented in the literature is given in weight fractions and a conversion must be made.
3. A table of the computed liquid-liquid equilibrium tie-line compositions and values of the parameters used in a specific model.
4. A figure of the ternary system showing the experimental and computed tie-lines.
5. A figure showing the computed and experimental values of the slopes of the tie-lines.

The pertinent data for the component binary systems along with some discussions of the binary systems are found in the Appendices. It is noted that the physical property data for the pure components generally came from reference (102) for hydrocarbons and reference (103) for other

components. Each component of the ternary system is designated by the numbers, (1), (2), and (3) in the table headings to facilitate the variable descriptions in terms of subscripts within the tables. The phases are arbitrarily designated as Alpha and Beta phase for identification purposes and to avoid any physical connotations. The basic equations for the various models discussed in this chapter are equations (37), (38), and (39). The Margules model implies that the parameters, $q_1$, $q_2$, $q_3$, are set equal to one in these basic equations. The Scatchard-Hamer model means that the parameters, $q_1$, $q_2$, $q_3$, are set equal to the molal volumes of components one, two and three, respectively, in the basic equations. The van Laar model means that the ratios of the q's are set equal to the ratios of the A's and furthermore the parameters $D_{12}$, $D_{23}$, and $D_{13}$ are set equal to zero in equations (37) through (39).

The system: furfural--n-heptane--cyclohexane.--The ternary system furfural--n-heptane--cyclohexane was studied at temperatures of 30, 60, and 90° C. by Bethea (41) and at 30° C. by Pennington and Marwil (42). There were no vapor-liquid equilibrium data available at these temperatures for the partially mixcible binary pairs, furfural--n-heptane and furfural--cyclohexane. The parameters for these systems were computed from mutual solubility data. The binary system, cyclohexane--n-heptane was considered to be an ideal system and therefore the parameters were set equal to zero for the prediction computations. A more detailed treatment of these binary systems is presented in Appendix D.

The results of the prediction of ternary tie-line data are given in Tables 4 through 9 and in Figures 5 through 10. The two parameter forms of the standard binary equations were used in equations (37), (38),

Table 3. Experimental Tie-line Data for the System: Furfural (1)--n-heptane (2)--cyclohexane (3) at 30° C. (Data of reference (41)).

| Tie-line | Alpha Phase Composition | | | Beta Phase Composition | | |
|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | $x_1$ | $x_2$ | $x_3$ |
| 1. | 0.856 | 0.0 | 0.144 | 0.065 | 0.0 | 0.935 |
| 2. | 0.922 | 0.0498 | 0.0282 | 0.060 | 0.7106 | 0.2294 |
| 3. | 0.903 | 0.0353 | 0.0617 | 0.064 | 0.4727 | 0.4633 |
| 4. | 0.877 | 0.0155 | 0.1075 | 0.063 | 0.1921 | 0.7449 |
| 5. | 0.940 | 0.060 | 0.0 | 0.060 | 0.940 | 0.0 |
| 6. | 0.915 | 0.0441 | 0.0409 | 0.063 | 0.6184 | 0.3186 |
| 7. | 0.904 | 0.0354 | 0.0606 | 0.066 | 0.4838 | 0.4502 |
| 8. | 0.943 | 0.057 | 0.0 | 0.060 | 0.940 | 0.0 |
| 9. | 0.851 | 0.0 | 0.149 | 0.0642 | 0.0 | 0.9358 |

Table 4. Computed Tie-line Values Using the van Laar Model for the System: Furfural (1)--n-heptane (2)--cyclohexane (3) at 30° C.

I. Values of the Constants Used.

| | | |
|---|---|---|
| $A_{12} = 1.340$ | $A_{13} = 1.357$ | $A_{23} = 0$ |
| $A_{21} = 1.359$ | $A_{31} = 1.025$ | $A_{32} = 0$ |
| $D_{12} = 0$ | $D_{12} = 0$ | $D_{23} = 0$ |
| $C_1 = 0$ | $C_2 = 0$ | $C_3 = 0$ |

II. Computed Tie-lines and Activities.

| Tie-line | Alpha Phase Composition<br>Beta Phase Composition | | | Computed Activities in Each Phase | | |
|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | $a_1$ | $a_2$ | $a_3$ |
| 1. | 0.934 | 0.056 | 0.010 | 0.946 | 0.866 | 0.085 |
| | 0.065 | 0.860 | 0.075 | 0.963 | 0.871 | 0.086 |
| 2. | 0.927 | 0.053 | 0.020 | 0.941 | 0.798 | 0.165 |
| | 0.065 | 0.790 | 0.145 | 0.956 | 0.801 | 0.166 |
| 3. | 0.921 | 0.049 | 0.030 | 0.936 | 0.721 | 0.255 |
| | 0.065 | 0.710 | 0.225 | 0.954 | 0.720 | 0.257 |
| 4. | 0.915 | 0.045 | 0.040 | 0.932 | 0.648 | 0.331 |
| | 0.065 | 0.640 | 0.295 | 0.949 | 0.649 | 0.334 |
| 5. | 0.906 | 0.044 | 0.050 | 0.925 | 0.612 | 0.382 |
| | 0.065 | 0.600 | 0.335 | 0.937 | 0.609 | 0.377 |
| 6. | 0.894 | 0.036 | 0.070 | 0.917 | 0.480 | 0.509 |
| | 0.065 | 0.475 | 0.400 | 0.924 | 0.483 | 0.510 |
| 7. | 0.875 | 0.025 | 0.100 | 0.904 | 0.311 | 0.674 |
| | 0.065 | 0.315 | 0.620 | 0.906 | 0.321 | 0.672 |

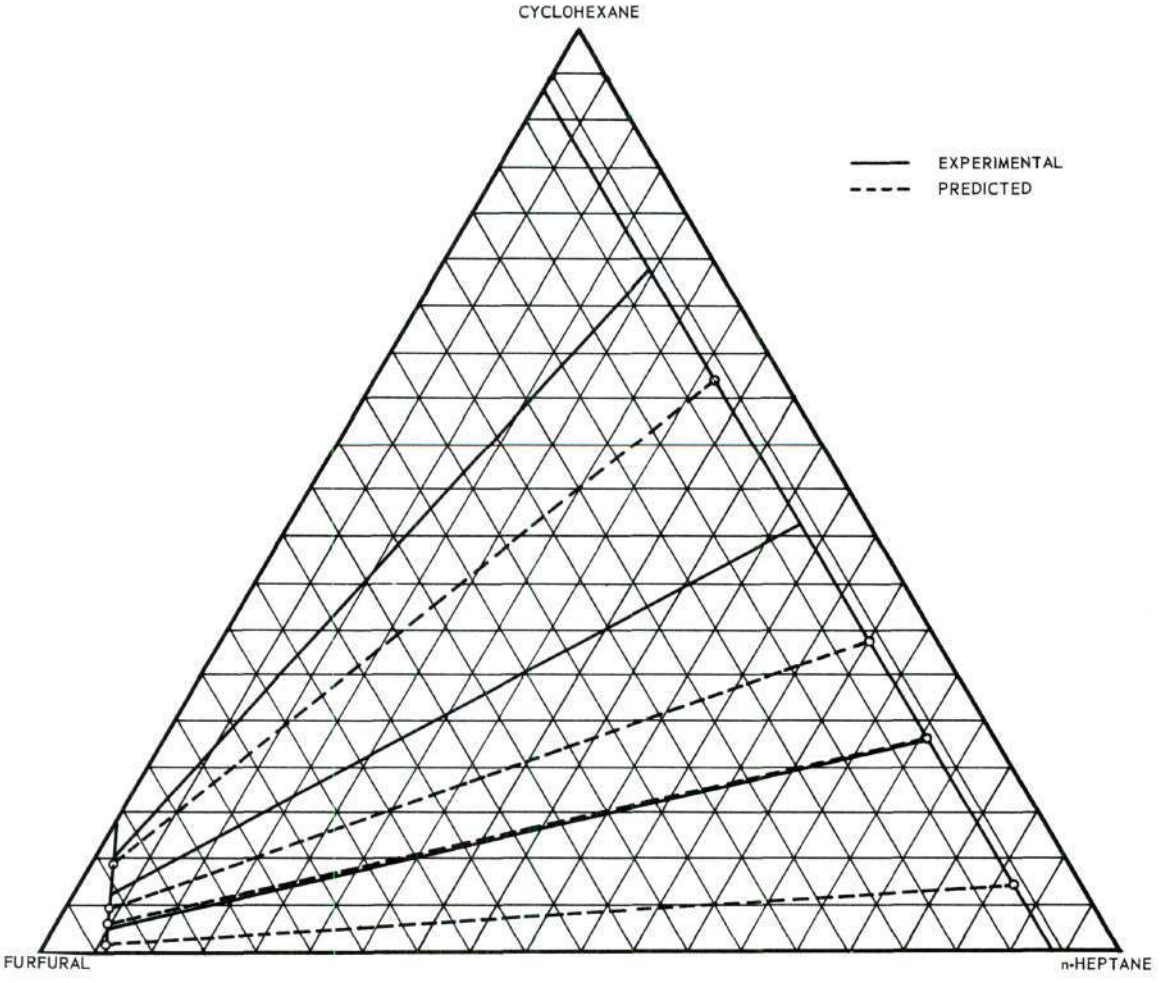


Figure 5. Experimental and computed liquid-liquid equilibrium using the van Laar model for the system: furfurall--n-heptane--cyclohexane at 30°C..

Table 5. Computed Tie-line Values Using the Margules Model for the System: Furfural (1)--n-heptane (2)--cyclohexane (3) at 30° C.

I. Values of the Constants Used.

| | | |
|---|---|---|
| $A_{12} = 1.376$ | $A_{13} = 1.345$ | $A_{23} = 0$ |
| $A_{21} = 1.357$ | $A_{31} = 1.016$ | $A_{32} = 0$ |
| $D_{12} = 0$ | $D_{13} = 0$ | $D_{23} = 0$ |
| $C_1 = 0$ | $C_2 = 3$ | $C_3 = 0$ |
| $q_1 = 1.0$ | $q_2 = 1.0$ | $q_3 = 1.0$ |

II. Computed Tie-lines and Activities

| Tie-line | Alpha Phase Composition<br>Beta Phase Composition | | | Computed Activities in Each Phase | | |
|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | $a_1$ | $a_2$ | $a_3$ |
| 1. | 0.928 | 0.052 | 0.020 | 0.942 | 0.790 | 0.157 |
| | 0.060 | 0.780 | 0.160 | 0.958 | 0.790 | 0.161 |
| 2. | 0.922 | 0.048 | 0.030 | 0.937 | 0.713 | 0.232 |
| | 0.060 | 0.705 | 0.235 | 0.948 | 0.715 | 0.237 |
| 3. | 0.915 | 0.045 | 0.040 | 0.932 | 0.650 | 0.304 |
| | 0.060 | 0.640 | 0.300 | 0.939 | 0.649 | 0.302 |
| 4. | 0.903 | 0.037 | 0.060 | 0.923 | 0.510 | 0.443 |
| | 0.060 | 0.500 | 0.440 | 0.907 | 0.506 | 0.445 |
| 5. | 0.890 | 0.030 | 0.080 | 0.913 | 0.393 | 0.572 |
| | 0.060 | 0.250 | 0.690 | 0.893 | 0.254 | 0.567 |
| 6. | 0.880 | 0.020 | 0.100 | 0.906 | 0.254 | 0.700 |
| | 0.060 | 0.250 | 0.690 | 0.893 | 0.254 | 0.699 |
| 7. | 0.869 | 0.011 | 0.120 | 0.898 | 0.134 | 0.819 |
| | 0.060 | 0.130 | 0.810 | 0.885 | 0.132 | 0.821 |

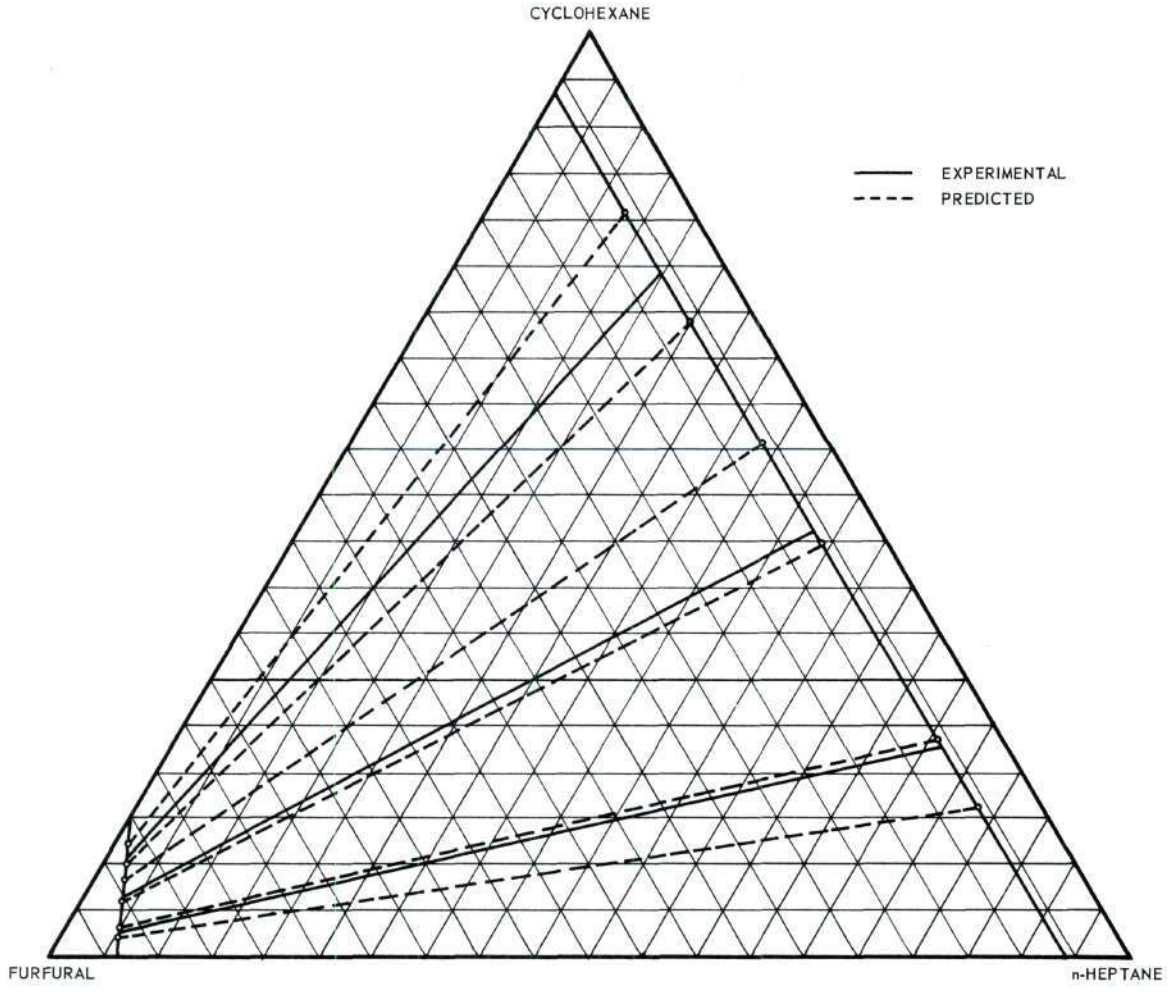


Figure 6. Experimental and computed liquid-liquid equilibrium using the Margules model for the system: furfural--n-heptane--cyclohexane at 30°C.

Table 6. Computed Tie-line Values Using the Scatchard-Hamer Model for the System: Furfural (1)--n-heptane (2)--Cyclohexane (3) at 30° C.

I. Values of the Constants Used.

| | | |
|---|---|---|
| $A_{12} = 1.340$ | $A_{13} = 1.321$ | $A_{23} = 0$ |
| $A_{21} = 1.265$ | $A_{31} = 0.876$ | $A_{32} = 0$ |
| $D_{12} = 0$ | $D_{13} = 0$ | $D_{23} = 0$ |
| $C_1 = 0$ | $C_2 = 0$ | $C_3 = 0$ |
| $q_1 = 0.084$ | $q_2 = 0.148$ | $q_3 = 0.110$ |

II. Computed Tie-lines and Activities.

| Tie-line | Alpha Phase Composition<br>Beta Phase Composition | | | Computed Activities in Each Phase | | |
|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | $a_1$ | $a_2$ | $a_3$ |
| 1. | 0.924 | 0.056 | 0.020 | 0.933 | 0.825 | 0.116 |
| | 0.068 | 0.810 | 0.122 | 0.929 | 0.827 | 0.116 |
| 2. | 0.932 | 0.058 | 0.010 | 0.940 | 0.888 | 0.058 |
| | 0.064 | 0.870 | 0.066 | 0.943 | 0.883 | 0.063 |
| 3. | 0.901 | 0.049 | 0.050 | 0.917 | 0.640 | 0.292 |
| | 0.084 | 0.618 | 0.298 | 0.917 | 0.641 | 0.292 |
| 4. | 0.895 | 0.045 | 0.060 | 0.912 | 0.568 | 0.352 |
| | 0.090 | 0.548 | 0.362 | 0.917 | 0.571 | 0.358 |
| 5. | 0.880 | 0.040 | 0.080 | 0.900 | 0.465 | 0.466 |
| | 0.094 | 0.448 | 0.458 | 0.899 | 0.465 | 0.462 |
| 6. | 0.869 | 0.031 | 0.100 | 0.891 | 0.334 | 0.588 |
| | 0.098 | 0.328 | 0.574 | 0.899 | 0.335 | 0.590 |

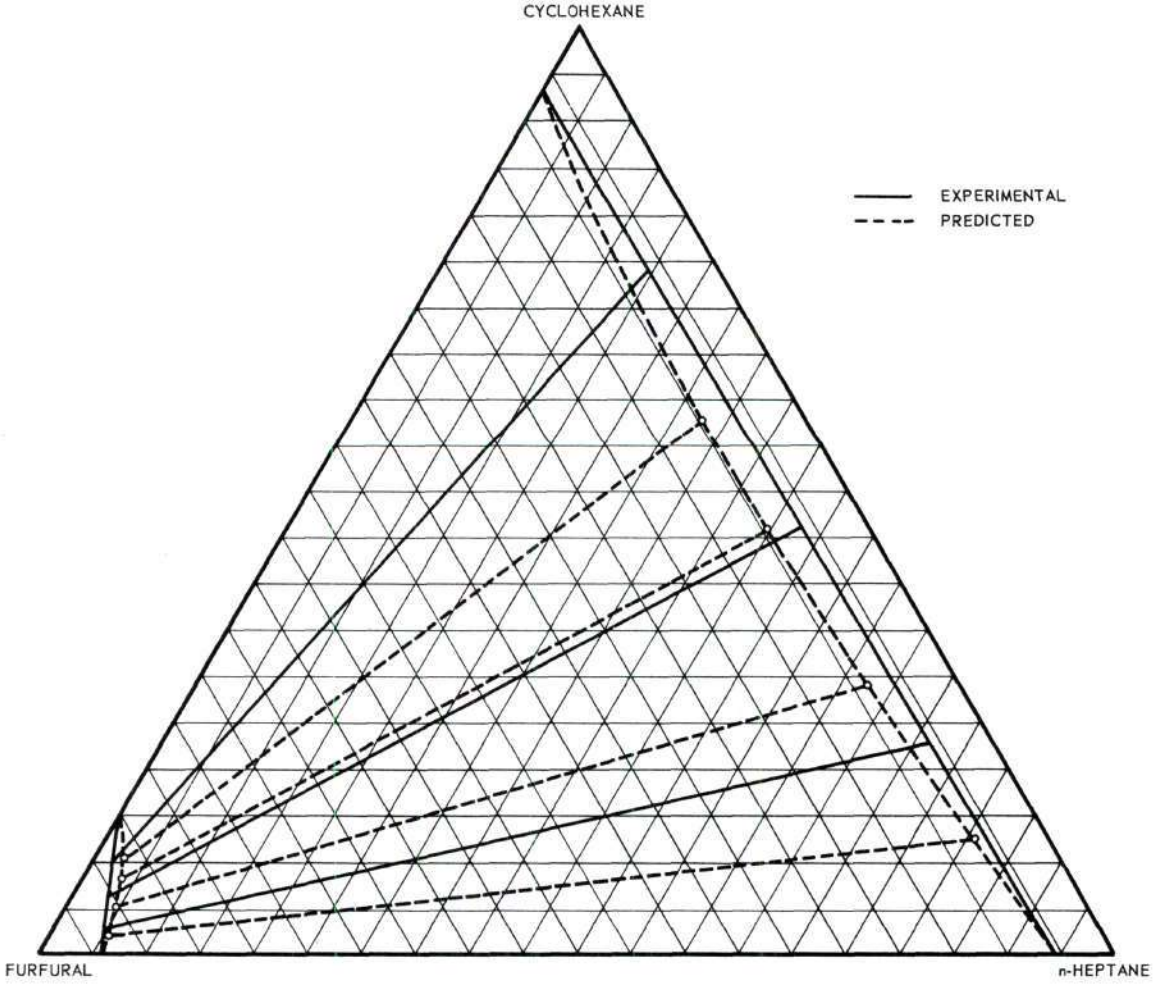


Figure 7. Experimental and computed liquid-liquid equilibrium using the Scatchard-Hamer model for the system: furfural--n-heptane--cyclohexane at 30°C.

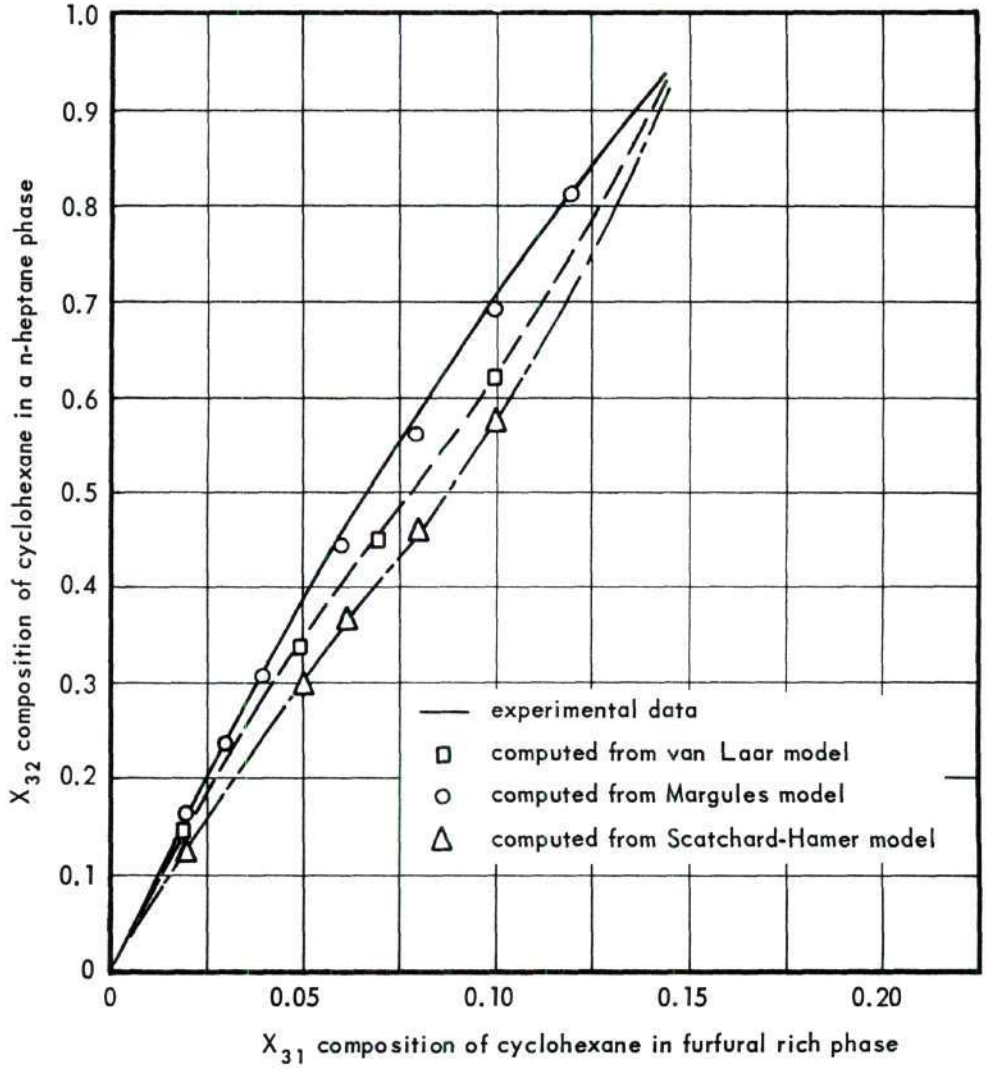


Figure 8. Experimental and computed distribution curves using the various models for the system: furfural--n-heptane--cyclohexane at 30°C.

Table 7. Computed Tie-line Values Using the van Laar Model for the System: Furfural (1)--n-heptane (2)--cyclohexane (3) at 60° C.

I. Values of the Constants Used.

| | | |
|---|---|---|
| $A_{12} = 1.103$ | $A_{13} = 1.031$ | $A_{23} = 0$ |
| $A_{21} = 1.167$ | $A_{31} = 0.854$ | $A_{32} = 0$ |
| $D_{12} = 0$ | $D_{13} = 0$ | $D_{23} = 0$ |
| $C_1 = 0$ | $C_2 = 0$ | $C_3 = 0$ |

II. Computed Tie-lines and Activities

| Tie-line | Alpha Phase Composition<br>Beta Phase Composition | | | Computed Activities in Each Phase | | |
|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | $a_1$ | $a_2$ | $a_3$ |
| 1. | 0.874 | 0.106 | 0.020 | 0.911 | 0.818 | 0.108 |
| | 0.135 | 0.780 | 0.085 | 0.910 | 0.818 | 0.108 |
| 2. | 0.853 | 0.097 | 0.050 | 0.898 | 0.698 | 0.251 |
| | 0.140 | 0.660 | 0.200 | 0.897 | 0.698 | 0.251 |
| 3. | 0.831 | 0.089 | 0.080 | 0.886 | 0.594 | 0.372 |
| | 0.145 | 0.555 | 0.300 | 0.885 | 0.592 | 0.373 |
| 4. | 0.781 | 0.069 | 0.150 | 0.847 | 0.492 | 0.496 |
| | 0.112 | 0.383 | 0.505 | 0.851 | 0.490 | 0.498 |
| 5. | 0.749 | 0.051 | 0.200 | 0.823 | 0.401 | 0.611 |
| | 0.176 | 0.214 | 0.610 | 0.829 | 0.408 | 0.609 |

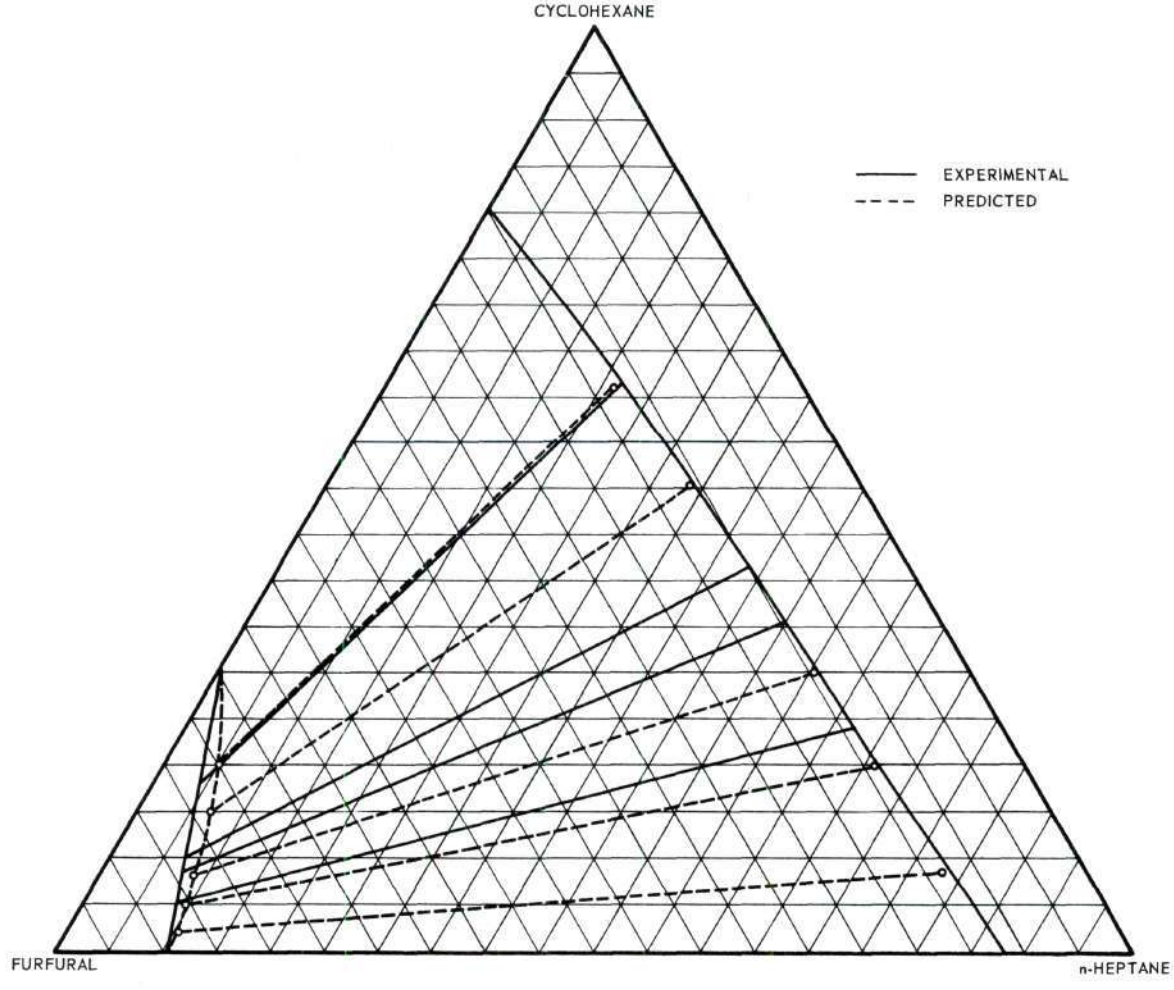


Figure 9. Experimental and computed liquid-liquid equilibrium using the van Laar model for the system: furfural--n-heptane--cyclohexane at 60°C.

Table 8. Computed Tie-line Values Using the Margules Model for the Systems: Furfural (1)--n-heptane (2)--cyclohexane (3) at 60° C.

I. Values of the Constants Used.

| | | |
|---|---|---|
| $A_{12} = 1.099$ | $A_{13} = 1.025$ | $A_{23} = 0$ |
| $A_{21} = 1.168$ | $A_{31} = 0.843$ | $A_{32} = 0$ |
| $D_{12} = 0$ | $D_{13} = 0$ | $D_{23} = 0$ |
| $C_1 = 0$ | $C_2 = 0$ | $C_3 = 0$ |
| $q_1 = 1.0$ | $q_2 = 1.0$ | $q_3 = 1.0$ |

II. Computed Tie-lines and Activities

| Tie-line | Alpha Phase Composition / Beta Phase Composition | | | Computed Activities in Each Phase | | |
|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | $a_1$ | $a_2$ | $a_3$ |
| 1. | 0.861 | 0.099 | 0.040 | 0.927 | 0.803 | 0.118 |
| | 0.140 | 0.701 | 0.159 | 0.925 | 0.805 | 0.120 |
| 2. | 0.818 | 0.082 | 0.100 | 0.873 | 0.581 | 0.384 |
| | 0.154 | 0.464 | 0.382 | 0.875 | 0.580 | 0.386 |
| 3. | 0.783 | 0.067 | 0.150 | 0.839 | 0.488 | 0.484 |
| | 0.116 | 0.375 | 0.509 | 0.837 | 0.491 | 0.486 |

Table 9. Computed Tie-line Values Using the van Laar Model for the System: Furfural (1)--n-heptane (2)--Cyclohexane (3) at 90° C.

I. Values of the Constants Used.

| | | |
|---|---|---|
| $A_{12} = 0.845$ | $A_{13} = 0.755$ | $A_{23} = 0$ |
| $A_{21} = 0.976$ | $A_{31} = 0.705$ | $A_{32} = 0$ |
| $D_{12} = 0$ | $D_{13} = 0$ | $D_{23} = 0$ |
| $C_1 = 0$ | $C_2 = 0$ | $C_3 = 0$ |

II. Computed Tie-lines and Activities

| Tie-line | Alpha Phase Composition<br>Beta Phase Composition | | | Computed Activities in Each Phase | | |
|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | $a_1$ | $a_2$ | $a_3$ |
| 1. | 0.726 | 0.264 | 0.010 | 0.916 | 0.796 | 0.167 |
| | 0.371 | 0.611 | 0.018 | 0.914 | 0.796 | 0.166 |
| 2. | 0.704 | 0.276 | 0.020 | 0.901 | 0.781 | 0.185 |
| | 0.376 | 0.590 | 0.034 | 0.099 | 0.780 | 0.186 |
| 3. | 0.688 | 0.282 | 0.030 | 0.887 | 0.764 | 0.199 |
| | 0.383 | 0.568 | 0.049 | 0.888 | 0.765 | 0.200 |

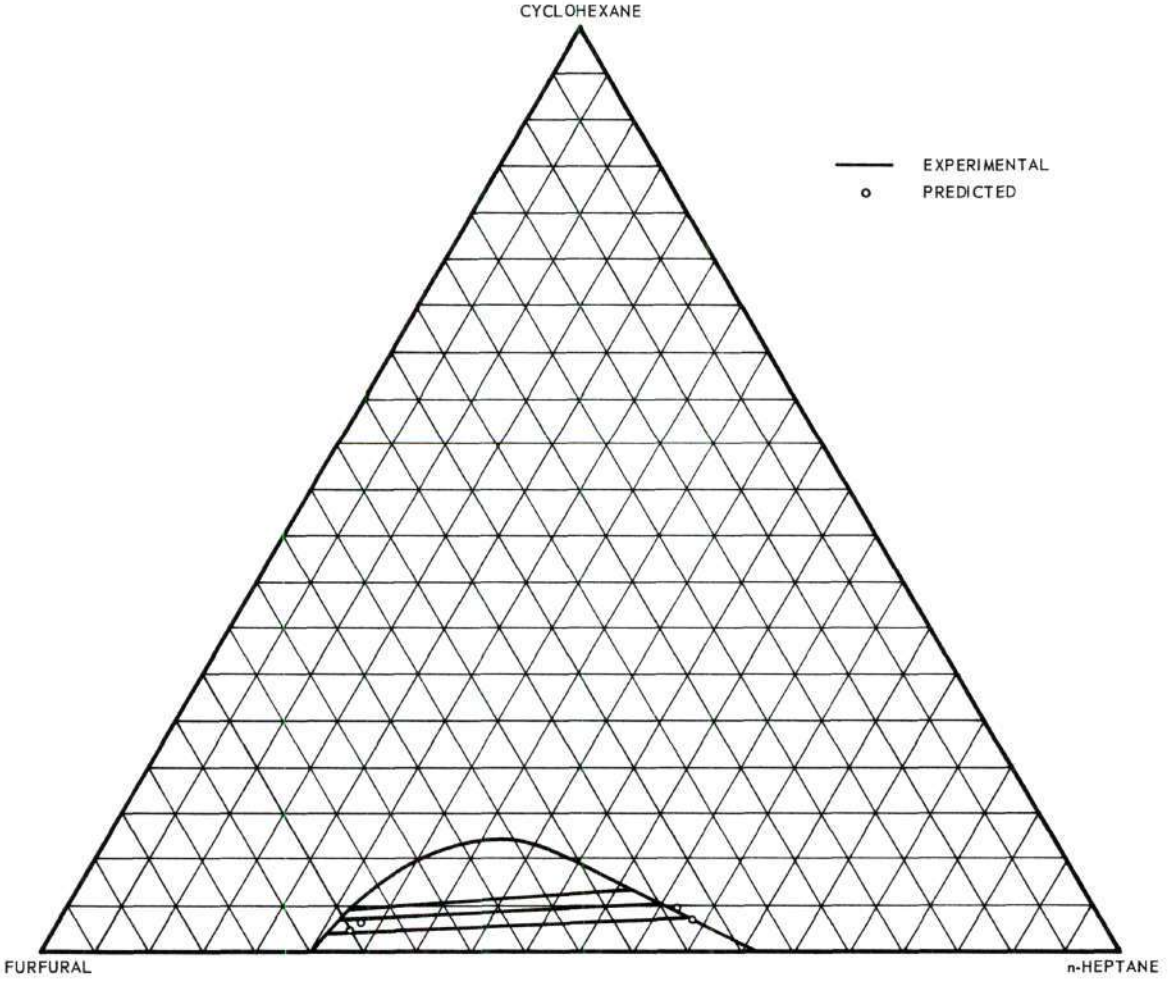


Figure 10. Experimental and computed liquid-liquid equilibrium using the van Laar model for the system: furfural--n-heptane--cyclohexane at 90°C.

and (39) the prediction of the system at 30° C. As can be seen in Figures 5 and 6, the computed results compare favorably with the experimental data for the Margules and van Laar ternary models. Figure 8 tends to show that the Margules model is better for the prediction of the ternary equilibrium than any of the other models studied. The Scatchard-Hamer equations did not predict well for this system. As the temperature of the system increased the predictions became poorer as can be seen from Figures 9 and 10. The Margules model gave essentially the same results as the van Laar models for Figures 9 and 10 and is not shown. Since the parameters are determined from mutual solubility data only, it is reasonable to expect that the values of the parameters become more uncertain in the region of the critical solution temperatures of the binary systems. It would be worthwhile to investigate the vapor-liquid equilibrium of a partially miscible binary system under isothermal conditions in the region of the critical solution temperature.

The system: aniline--n-heptane--cyclohexane.--The ternary liquid system, aniline--n-heptane--cyclohexane, was studied at 25° C. by Hunter and Brown (43). The results of the ternary predictions for this system are shown in Figures 11 and 12 for the Margules model. The van Laar model gave similar results and is not shown. Since this system is comparable to the furfural--n-heptane--cyclohexane ternary system, it was expected that the results would be comparable also. This was not the case, however, and the difficulty appears to be in obtaining suitable parameters for the binary system, aniline--cyclohexane. The computation of these parameters is discussed in Appendix D. As is discussed in the Appendix, there

Table 10. Experimental Tie-line Data for the System: Aniline (1)--n-heptane (2)--cyclohexane (3) at 25° C.

| Tie-line | Alpha Phase Composition | | | Beta Phase Composition | | |
|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | $x_1$ | $x_2$ | $x_3$ |
| 1. | 0.939 | 0.061 | 0.0 | 0.071 | 0.929 | 0.0 |
| 2. | 0.927 | 0.056 | 0.017 | 0.084 | 0.706 | 0.210 |
| 3. | 0.905 | 0.050 | 0.045 | 0.094 | 0.556 | 0.350 |
| 4. | 0.886 | 0.046 | 0.068 | 0.103 | 0.439 | 0.458 |
| 5. | 0.830 | 0.031 | 0.139 | 0.124 | 0.227 | 0.649 |
| 6. | 0.718 | 0.0 | 0.282 | 0.152 | 0.0 | 0.848 |

appears to be some conflicting data for the binary system, aniline -- cyclohexane which is probably reflected in the poor results of the computations for this system.

The system: nitroethane--n-octant--isooctane.--The liquid-liquid equilibrium data for this system were determined by the author and is discussed in Appendix E of this thesis. The results of the predictions are compared to the experimentally determined data at 25° C. in Figure 13. The Margules model gives a slightly better prediction of the ternary data than the van Laar equations. The discussion of the computation of the parameters to the binary equations is given in Appendix D.

Table 11. Computed Tie-line Values Using the Margules Model for the System: Aniline (1)--n-heptane (2)--cyclohexane (3) at 25° C.

I. Values of the Constants Used.

| | | |
|---|---|---|
| $A_{12} = 1.298$ | $A_{13} = 1.098$ | $A_{23} = 0$ |
| $A_{21} = 1.357$ | $A_{31} = 0.767$ | $A_{32} = 0$ |
| $D_{12} = 0$ | $D_{13} = 0$ | $D_{23} = 0$ |
| $C_1 = 0$ | $C_2 = 0$ | $C_3 = 0$ |
| $q_1 = 1.0$ | $q_2 = 1.0$ | $q_3 = 1.0$ |

II. Computed Tie-lines and Activities.

| Tie-line | Alpha Phase Composition<br>Beta Phase Composition | | | Computed Activities in Each Phase | | |
|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | $a_1$ | $a_2$ | $a_3$ |
| 1. | 0.934 | 0.056 | 0.010 | 0.947 | 0.844 | 0.084 |
| | 0.080 | 0.829 | 0.091 | 0.950 | 0.849 | 0.087 |
| 2. | 0.922 | 0.048 | 0.030 | 0.940 | 0.678 | 0.236 |
| | 0.090 | 0.648 | 0.262 | 0.941 | 0.683 | 0.241 |
| 3. | 0.867 | 0.033 | 0.100 | 0.918 | 0.256 | 0.622 |
| | 0.140 | 0.257 | 0.603 | 0.918 | 0.256 | 0.616 |
| 4. | 0.852 | 0.028 | 0.120 | 0.912 | 0.186 | 0.692 |
| | 0.205 | 0.143 | 0.652 | 0.902 | 0.184 | 0.678 |

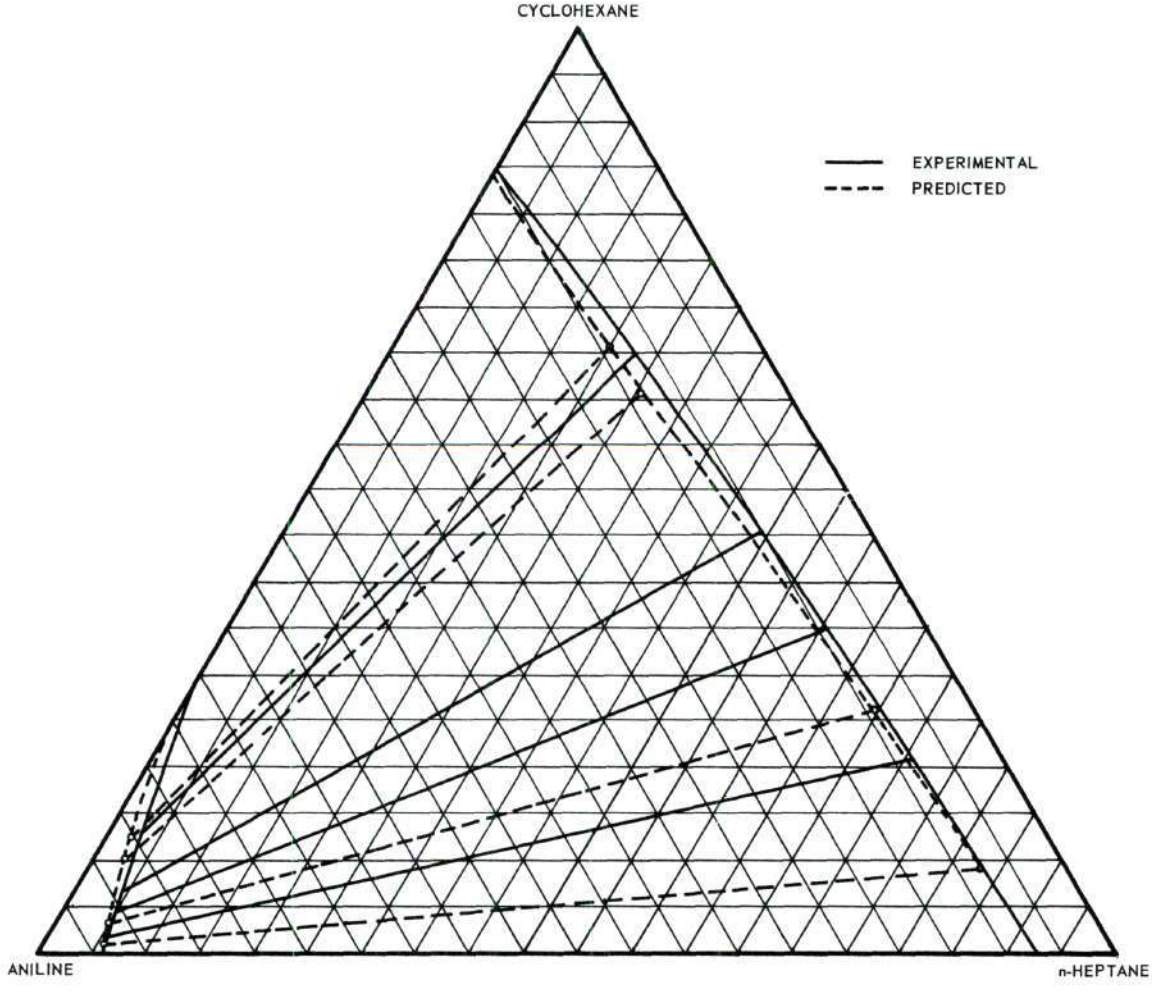


Figure 11. Experimental and computed liquid-liquid equilibrium using the Margules model for the system: aniline--n-heptane--cyclohexane at 25°C.

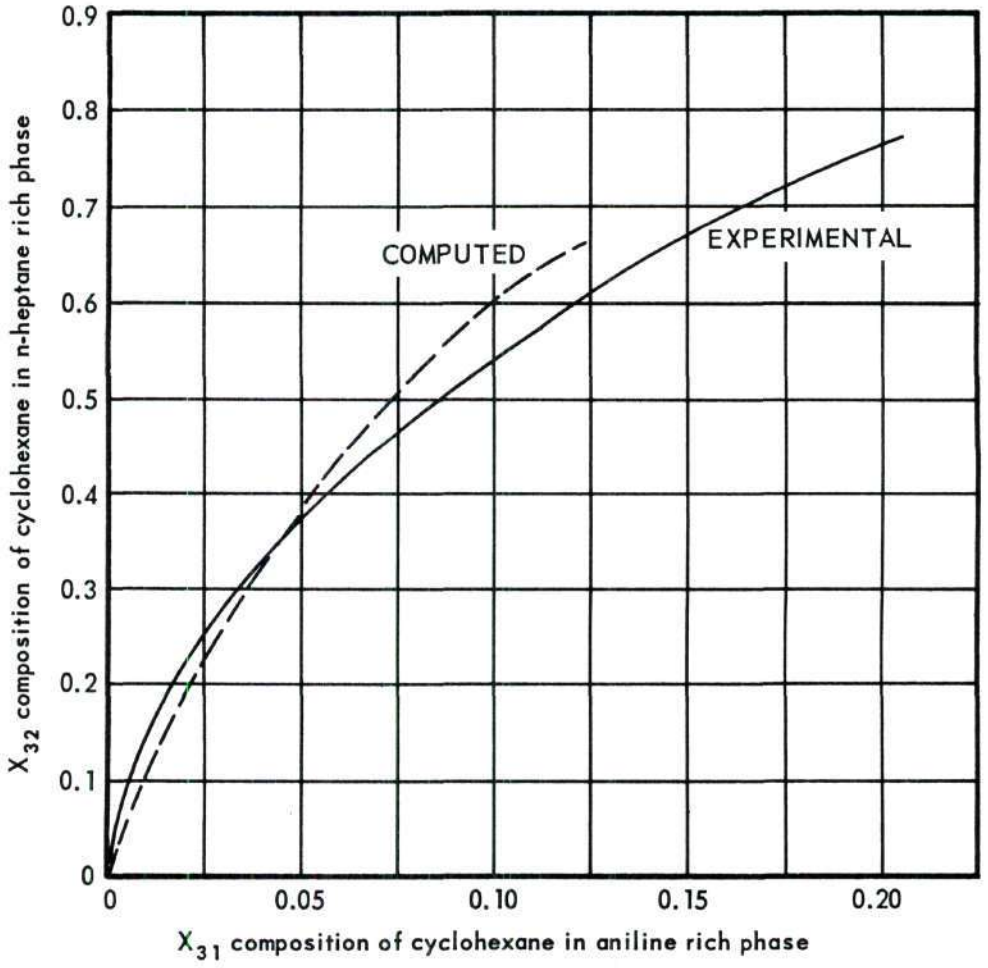


Figure 12. Experimental and computed distribution curves for the system: aniline--n-heptane--cyclohexane at 25°C.

Table 12. Experimental Tie-line Data for the System: Nitroethane (1)--n-octane (2)--isooctane (3) at 25°C.

| Tie-line | Alpha Phase Composition | | | Beta Phase Composition | | |
|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | $x_1$ | $x_2$ | $x_3$ |
| 1. | 0.878 | 0.110 | 0.012 | 0.194 | 0.734 | 0.072 |
| 2. | 0.856 | 0.085 | 0.059 | 0.210 | 0.482 | 0.308 |
| 3. | 0.831 | 0.061 | 0.108 | 0.235 | 0.307 | 0.458 |
| 4. | 0.794 | 0.0 | 0.206 | 0.305 | 0.0 | 0.695 |
| 5. | 0.880 | 0.120 | 0.0 | 0.190 | 0.810 | 0.0 |

The system: chloroform--water-acetone.--The liquid-liquid equilibrium data at 25° C. of Reinders and deMinjer (46) were used in this study of the ternary system, chloroform -- water -- acetone. The results of the predictions of the liquid-liquid equilibrium for this ternary system are summarized in Tables 16 and 17 and in Figures 14 and 15. The Margules three-constant model was used in these predictions since it gave the best fit to the data for the binary systems. The constants used in obtaining the data of Table 17 were evaluated by the automatic procedures discussed in the previous chapter. It was felt that the prediction indicated in Table 17, could be improved upon, and, as is discussed in Appendix D, the binary data were reevaluated and new parameters were determined. The results, shown in Table 16 and Figure 14 were better, but the prediction method failed to give a good representation of the ternary data in the region of the plait point. It is noted that the constant $D_{12}$ for the binary system, chloroform-water was arbitrarily chosen to cause the Margules

Table 13. Computed Tie-line Values Using the Margules Model for the System: Nitroethane (1)-- n-octane (2)--isooctane (3) at 25° C.

I. Values of the Constants Used.

| | | |
|---|---|---|
| $A_{12} = 0.974$ | $A_{13} = 0.866$ | $A_{23} = 0$ |
| $A_{21} = 1.154$ | $A_{31} = 1.018$ | $A_{32} = 0$ |
| $D_{12} = 0$ | $D_{13} = 0$ | $D_{23} = 0$ |
| $C_1 = 0$ | $C_2 = 0$ | $C_3 = 0$ |
| $q_1 = 1.0$ | $q_2 = 1.0$ | $q_3 = 1.0$ |

II. Computed Tie-lines and Activities.

| Tie-line | Alpha Phase Composition<br>Beta Phase Composition | | | Computed Activities in Each Phase | | |
|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | $a_1$ | $a_2$ | $a_3$ |
| 1. | 0.879 | 0.111 | 0.010 | 0.918 | 0.816 | 0.068 |
| | 0.190 | 0.756 | 0.054 | 0.918 | 0.815 | 0.068 |
| 2. | 0.854 | 0.096 | 0.050 | 0.908 | 0.618 | 0.322 |
| | 0.215 | 0.555 | 0.230 | 0.909 | 0.618 | 0.323 |
| 3. | 0.829 | 0.071 | 0.100 | 0.899 | 0.410 | 0.541 |
| | 0.235 | 0.357 | 0.408 | 0.897 | 0.411 | 0.541 |
| 4. | 0.806 | 0.044 | 0.150 | 0.891 | 0.231 | 0.693 |
| | 0.260 | 0.192 | 0.548 | 0.891 | 0.230 | 0.692 |

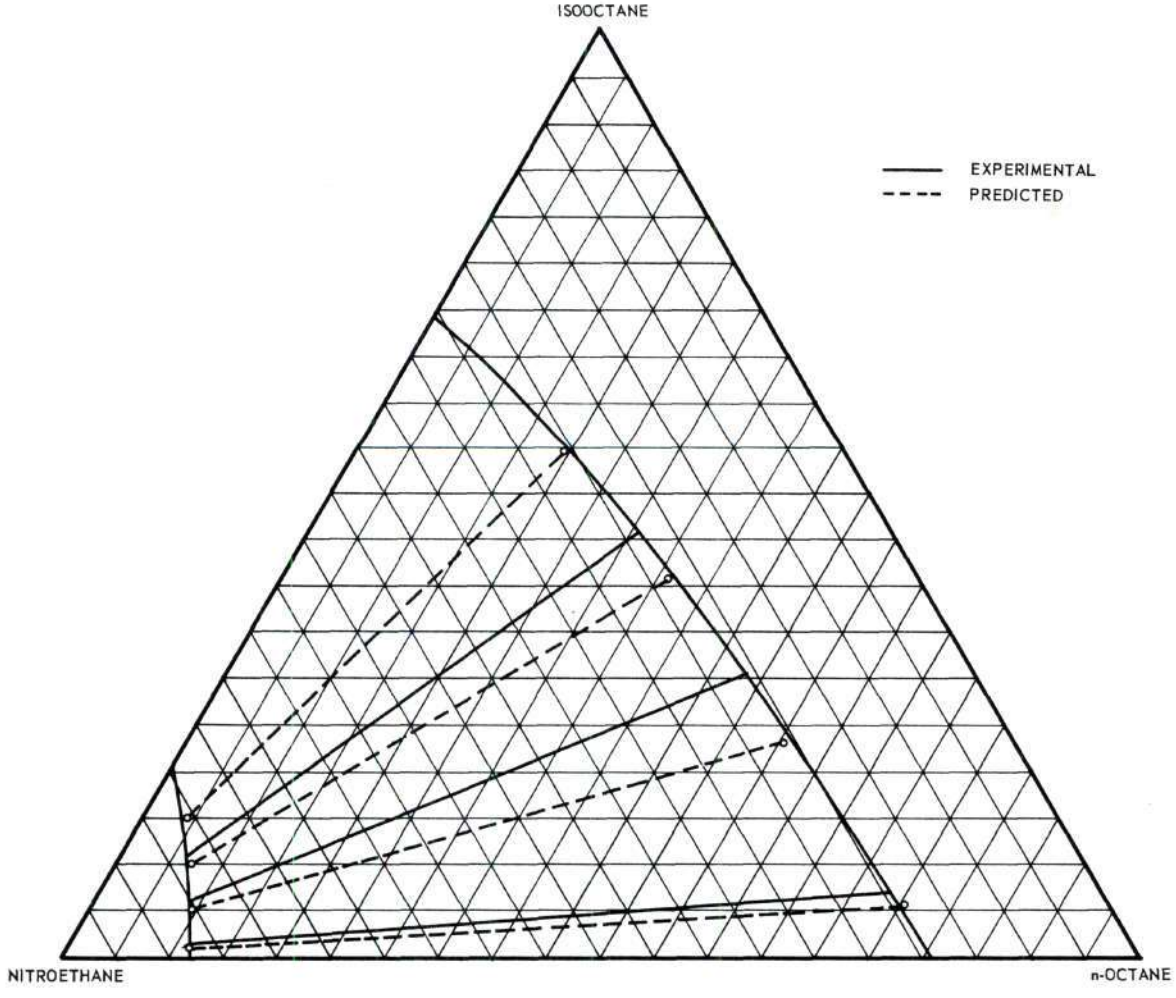


Figure 13. Experimental and computed liquid-liquid equilibrium using the Margules model for the system: nitroethane--n-octane--isooctane at 25°C.

Table 14. Computed Tie-line Values Using the van Laar Model for the System: Nitroethane (1)--n-octane (2)--isooctane (3) at 25° C.

I. Values of the Constants Used.

| | | |
|---|---|---|
| $A_{12} = 0.983$ | $A_{13} = 0.871$ | $A_{23} = 0$ |
| $A_{21} = 1.160$ | $A_{31} = 1.031$ | $A_{32} = 0$ |
| $D_{12} = 0$ | $D_{13} = 0$ | $D_{23} = 0$ |
| $C_1 = 0$ | $C_2 = 0$ | $C_3 = 0$ |

II. Computed Tie-lines and Activities.

| Tie-line | Alpha Phase Composition / Beta Phase Composition | | | Computed Activities in Each Phase | | |
|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | $a_1$ | $a_2$ | $a_3$ |
| 1. | 0.874 | 0.116 | 0.010 | 0.916 | 0.818 | 0.074 |
| | 0.195 | 0.755 | 0.050 | 0.916 | 0.818 | 0.073 |
| 2. | 0.865 | 0.105 | 0.030 | 0.912 | 0.711 | 0.208 |
| | 0.205 | 0.649 | 0.146 | 0.912 | 0.713 | 0.209 |
| 3. | 0.839 | 0.081 | 0.080 | 0.903 | 0.489 | 0.464 |
| | 0.230 | 0.430 | 0.340 | 0.905 | 0.490 | 0.464 |
| 4. | 0.820 | 0.060 | 0.120 | 0.896 | 0.334 | 0.609 |
| | 0.245 | 0.287 | 0.468 | 0.894 | 0.335 | 0.608 |
| 5. | 0.793 | 0.027 | 0.180 | 0.888 | 0.134 | 0.760 |
| | 0.270 | 0.110 | 0.620 | 0.884 | 0.134 | 0.757 |

equations to follow the reciprocal liquid composition function in the manner discussed for the binary system, benzene -- water in Appendix D. The results as given in Table 16 are good in the dilute acetone regions considering that this system is made up of an extremely immiscible binary pair (chloroform -- water) and a system which shows negative deviations from Raoult's law (acetone -- chloroform). A single tie-line was computed using the van Laar model and another using the Scatchard-Hamer model. These tie-lines predicted a more non-ideal system than that predicted by the Margules model and therefore no further computations were made with equations other than the Margules.

The system: benzene--water--pyridine.--The ternary liquid-liquid equilibrium for the system, benzene--water--pyridine has been studied by Smith et al. (47) at several different temperatures. In this work, this system was studied theoretically at 60° C. because this was close to the temperatures for which the component binary equilibrium data were available. When the ternary data are plotted in a weight fraction basis, it is observed that the slopes of the tie-lines change in direction as the concentration of pyridine increases. Systems exhibiting such behavior are called "solutropes" (47). When the data were converted to mol fractions, the slopes of the tie-lines did not change as the concentration of pyridine increased.

A most striking feature of this system is the low flat binodal curve with an extremely immiscible binary pair such as benzene-water. This would indicate that the ternary system tends toward an ideal solution very quickly with small increases in pyridine concentration. This fact would put any approximating function to a very severe test. The binary system, benzene--pyridine is almost ideal with only a slight positive

Table 15. Experimental Tie-line Data for the System: Chloroform (1)--Water (2)--Acetone (3) at 25° C.

| Tie-line | Alpha Phase Composition | | | Beta Phase Composition | | |
|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | $x_1$ | $x_2$ | $x_3$ |
| 1. | 753 | 0.029 | 0.218 | 0.001 | 0.784 | 0.015 |
| 2. | 0.649 | 0.037 | 0.314 | 0.002 | 0.967 | 0.031 |
| 3. | 0.563 | 0.045 | 0.392 | 0.002 | 0.951 | 0.047 |
| 4. | 0.500 | 0.058 | 0.442 | 0.002 | 0.936 | 0.062 |
| 5. | 0.382 | 0.087 | 0.531 | 0.002 | 0.906 | 0.092 |
| 6. | 0.313 | 0.121 | 0.566 | 0.002 | 0.882 | 0.116 |
| 7. | 0.301 | 0.127 | 0.572 | 0.002 | 0.877 | 0.121 |
| 8. | 0.265 | 0.151 | 0.584 | 0.003 | 0.863 | 0.134 |
| 9. | 0.239 | 0.172 | 0.589 | 0.003 | 0.845 | 0.152 |
| 10. | 0.211 | 0.199 | 0.590 | 0.004 | 0.826 | 0.170 |
| 11. | 0.185 | 0.225 | 0.590 | 0.005 | 0.809 | 0.186 |
| 12. | 0.165 | 0.252 | 0.583 | 0.008 | 0.786 | 0.206 |
| 13. | 0.157 | 0.266 | 0.577 | 0.009 | 0.776 | 0.214 |
| 14. | 0.143 | 0.289 | 0.568 | 0.009 | 0.766 | 0.225 |
| 15. | 0.123 | 0.331 | 0.546 | 0.012 | 0.751 | -.237 |
| 16. | 0.118 | 0.341 | 0.541 | 0.012 | 0.742 | 0.246 |
| 17. | 0.083 | 0.439 | 0.478 | 0.020 | 0.692 | 0.288 |
| 18. | 0.064 | 0.499 | 0.437 | 0.028 | 0.647 | 0.325 |
| 19. | 0.044 | 0.573 | 0.383 | 0.044 | 0.573 | 0.383 |

Table 16. Computed Tie-line Values Using the Margules Model for the System: Chloroform (1)--Water (2)--Acetone (3) at 25° C.

I. Values of the Constants Used.

| | | |
|---|---|---|
| $A_{12} = 2.86$ | $A_{13} = 0.305$ | $A_{23} = 0.640$ |
| $A_{21} = 1.95$ | $A_{31} = 0.370$ | $A_{32} = 0.845$ |
| $D_{12} = 6.40$ | $D_{13} = 0.130$ | $D_{23} = 0.620$ |
| $C_1 = 0$ | $C_2 = 0$ | $C_3 = 0$ |
| $q_1 = 1.0$ | $q_2 = 1.0$ | $q_3 = 1.0$ |

II. Computed Tie-lines and Activities.

| Tie-line | Alpha Phase Composition<br>Beta Phase Composition | | | Computed Activities in Each Phase | | |
|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | $a_1$ | $a_2$ | $a_3$ |
| 1. | 0.821 | 0.029 | 0.150 | 0.818 | 0.987 | 0.078 |
| | 0.0014 | 0.985 | 0.0136 | 0.822 | 0.986 | 0.087 |
| 2. | 0.715 | 0.035 | 0.250 | 0.692 | 0.976 | 0.150 |
| | 0.00135 | 0.972 | 0.02665 | 0.690 | 0.975 | 0.148 |
| 3. | 0.488 | 0.062 | 0.450 | 0.432 | 0.936 | 0.345 |
| | 0.0015 | 0.914 | 0.0845 | 0.419 | 0.937 | 0.332 |
| 4. | 0.425 | 0.075 | 0.500 | 0.369 | 0.917 | 0.402 |
| | 0.0020 | 0.872 | 0.126 | 0.367 | 0.918 | 0.400 |
| 5. | 0.384 | 0.086 | 0.530 | 0.332 | 0.904 | 0.438 |
| | 0.0025 | 0.837 | 0.1605 | 0.331 | 0.905 | 0.435 |
| 6. | 0.354 | 0.096 | 0.55 | 0.307 | 0.897 | 0.462 |
| | 0.003 | 0.809 | 0.188 | 0.306 | 0.896 | 0.457 |
| 7. | 0.324 | 0.106 | 0.570 | 0.283 | 0.883 | 0.487 |
| | 0.0045 | 0.756 | 0.2395 | 0.287 | 0.881 | 0.487 |
| 8. | 0.309 | 0.114 | 0.580 | 0.271 | 0.873 | 0.500 |
| | 0.0055 | 0.726 | 0.2685 | 0.271 | 0.873 | 0.501 |
| 9. | 0.272 | 0.128 | 0.600 | 0.246 | 0.859 | 0.527 |
| | 0.0075 | 0.678 | 0.3145 | 0.247 | 0.859 | 0.523 |
| 10. | 0.237 | 0.143 | 0.620 | 0.222 | 0.833 | 0.554 |
| | 0.0130 | 0.598 | 0.389 | 0.222 | 0.833 | 0.554 |

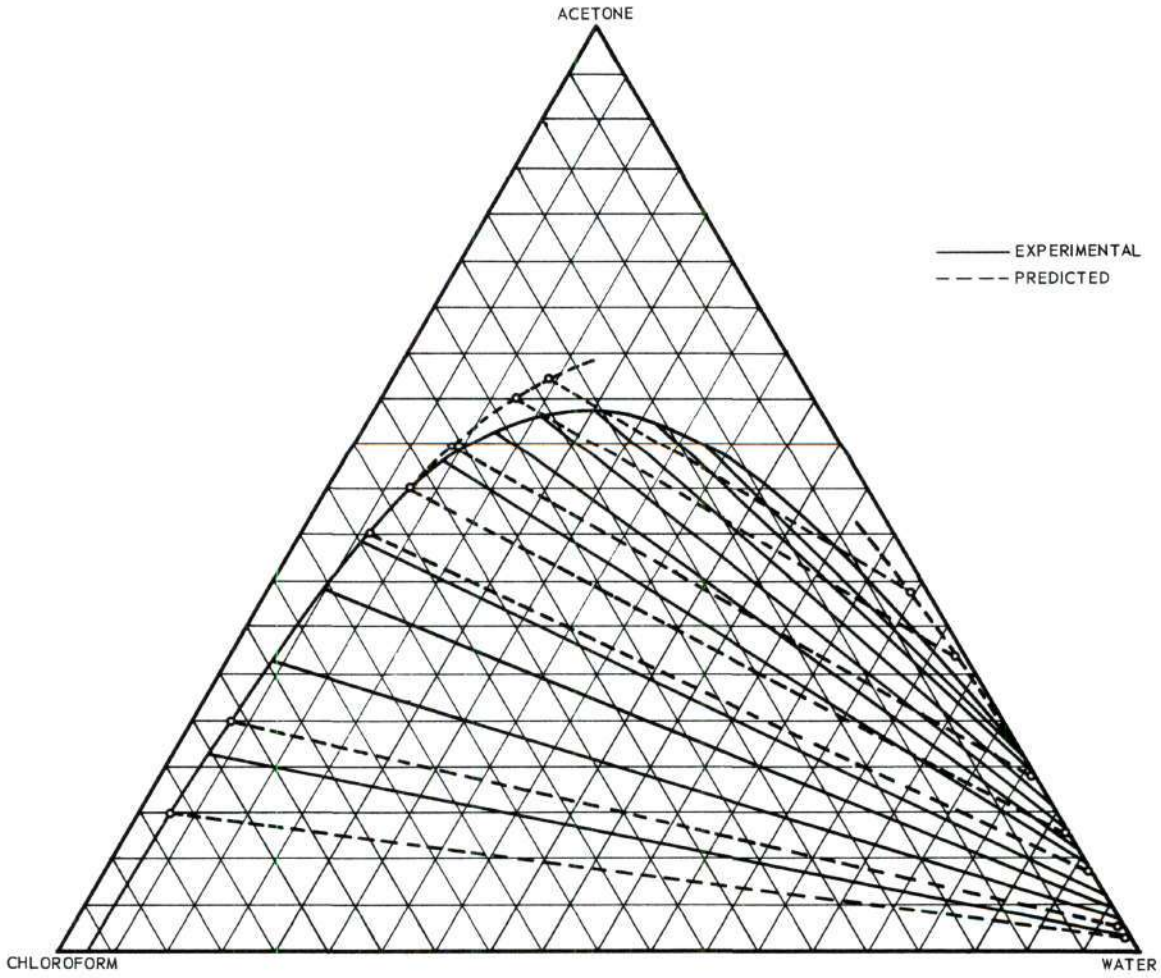


Figure 14. Experimental and computed liquid-liquid equilibrium using the Margules model for the system: chloroform--water--acetone at 25°C.

Table 17. Computed Tie-line Values Using the Margules Model for the System: Chloroform (1)--Water (2)--Acetone (3) at 25° C.

I. Values of the Constants Used.

| | | |
|---|---|---|
| $A_{12} = 2.86$ | $A_{13} = -0.205$ | $A_{23} = 0.838$ |
| $A_{21} = 1.95$ | $A_{31} = -0.348$ | $A_{32} = 0.843$ |
| $D_{12} = 0$ | $D_{13} = 0.167$ | $D_{23} = 0.148$ |
| $C_1 = 0$ | $C_2 = 0$ | $C_3 = 0$ |
| $q_1 = 1.0$ | $q_2 = 1.0$ | $q_3 = 1.0$ |

II. Computed Tie-lines and Activities

| Tie-line | Alphs Phase Composition / Beta Phase Composition | | | Computed Activities in Each Phase | | |
|---|---|---|---|---|---|---|
| 1. | 0.895 | 0.014 | 0.090 | 0.892 | 0.992 | 0.046 |
| | 0.0014 | 0.989 | 0.0096 | 0.902 | 0.990 | 0.059 |
| 2. | 0.8651 | 0.0149 | 0.120 | 0.8573 | 0.9931 | 0.0639 |
| | 0.0013 | 0.990 | 0.0087 | 0.8481 | 0.9910 | 0.0529 |
| 3. | 0.8343 | 0.0157 | 0.150 | 0.8216 | 0.9893 | 0.0836 |
| | 0.0013 | 0.9860 | 0.0127 | 0.8117 | 0.9872 | 0.0780 |
| 4. | 0.7828 | 0.0172 | 0.200 | 0.7601 | 0.9808 | 0.1201 |
| | 0.0013 | 0.980 | 0.0187 | 0.7601 | 0.9817 | 0.1138 |
| 5. | 0.730 | 0.0191 | 0.250 | 0.6968 | 0.9760 | 0.1611 |
| | 0.0013 | 0.972 | 0.0267 | 0.6968 | 0.9745 | 0.1586 |
| 6. | 0.6787 | 0.0213 | 0.300 | 0.6329 | 0.9660 | 0.2065 |
| | 0.0013 | 0.963 | 0.0357 | 0.6325 | 0.9668 | 0.2053 |
| 7. | 0.626 | 0.024 | 0.350 | 0.569, | 0.9554 | 0.2558 |
| | 0.0013 | 0.953 | 0.0457 | 0.5684 | 0.9587 | 0.2529 |

Table 17. (Continued)

II. Computed Tie-lines and Activities.

| Tie-line | Alpha Phase Composition<br>Beta Phase Composition | | | Computed Activities in Each Phase | | |
|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | $a_1$ | $a_2$ | $a_3$ |
| 8. | 0.572 | 0.028 | 0.400 | 0.5060 | 0.9620 | 0.3085 |
| | 0.0013 | 0.941 | 0.0577 | 0.5007 | 0.9494 | 0.3045 |
| 9. | 0.578 | 0.032 | 0.450 | 0.4453 | 0.9416 | 0.3641 |
| | 0.0014 | 0.924 | 0.0746 | 0.4508 | 0.9370 | 0.3686 |
| 10. | 0.462 | 0.038 | 0.500 | 0.3866 | 0.9372 | 0.4213 |
| | 0.0014 | 0.909 | 0.0896 | 0.3864 | 0.9270 | 0.4178 |
| 11. | 0.405 | 0.045 | 0.550 | 0.3310 | 0.9170 | 0.4800 |
| | 0.0015 | 0.887 | 0.115 | 0.3310 | 0.9133 | 0.4788 |
| 12. | 0.382 | 0.048 | 0.570 | 0.3097 | 0.9032 | 0.5034 |
| | 0.0015 | 0.879 | 0.1195 | 0.3055 | 0.9086 | 0.4983 |
| 13. | 0.357 | 0.053 | 0.590 | 0.2883 | 0.9071 | 0.5267 |
| | 0.0016 | 0.867 | 0.1314 | 0.2289 | 0.9021 | 0.5248 |
| 14. | 0.332 | 0.058 | 0.610 | 0.2675 | 0.9020 | 0.5501 |
| | 0.0017 | 0.854 | 0.1443 | 0.2670 | 0.8953 | 0.5505 |
| 15. | 0.307 | 0.063 | 0.630 | 0.2472 | 0.8894 | 0.5737 |
| | 0.0018 | 0.840 | 0.1582 | 0.2493 | 0.8885 | 0.5752 |
| 16. | 0.293 | 0.067 | 0.640 | 0.2368 | 0.8914 | 0.5854 |
| | 0.0017 | 0.839 | 0.1593 | 0.2336 | 0.8880 | 0.5774 |

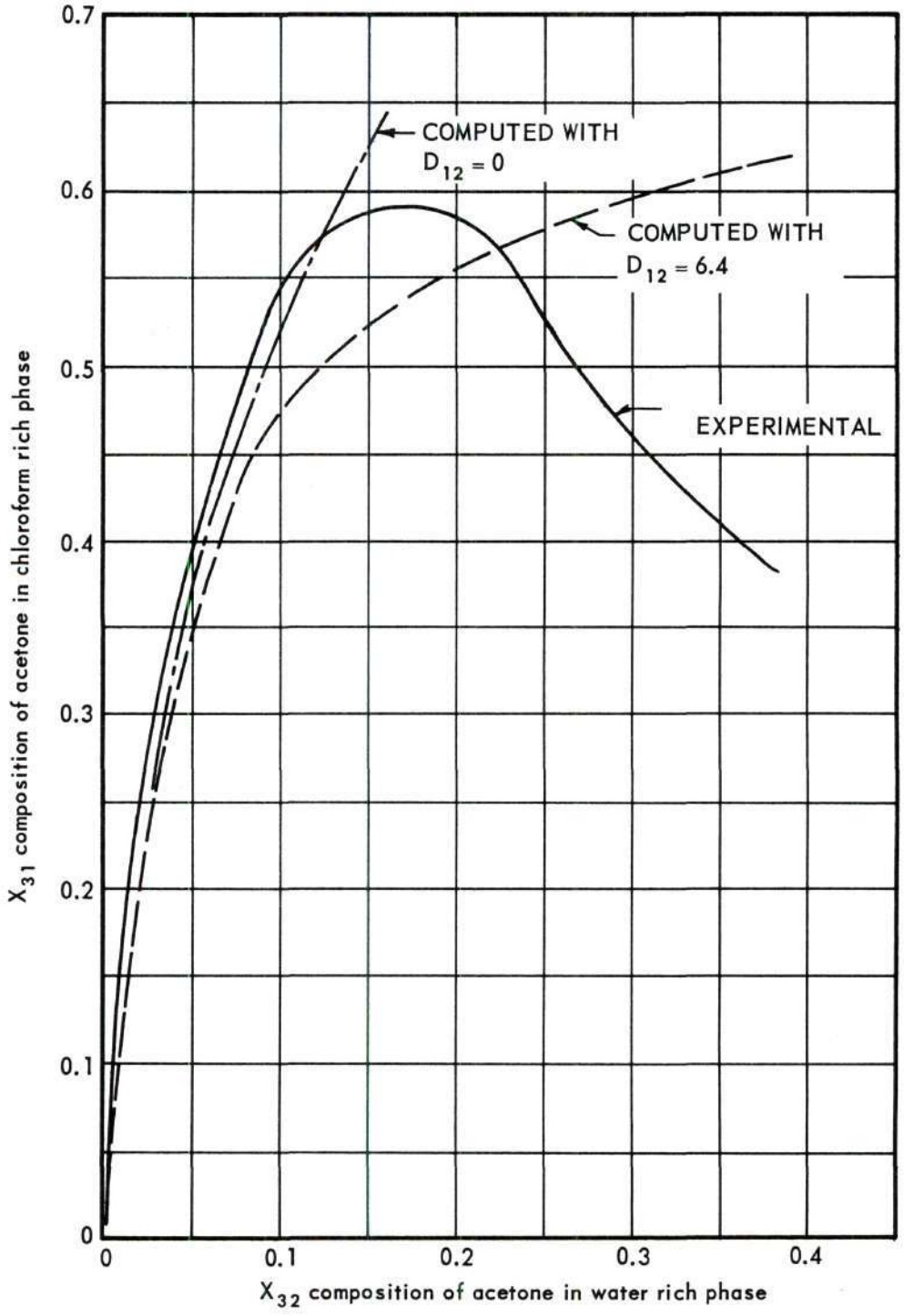


Figure 15. Experimental and computed distribution curves for the system: chloroform--water--acetone at 25°C.

deviation from Raoult's law. The binary system, pyridine--water shows a positive deviation from Raoult's law with an extreme deviation from ideality at low pyridine concentrations. These binary systems are discussed in Appendix D.

The tie-line results of the prediction using the Margules three-constant model are given in Table 19 and Figure 16. It was found that the binodal curve deviated considerably from the experimental curve and predicted a plait point at a much higher pyridine concentration than indicated by the experimental data. Thus it was concluded that the Margules model failed to give a satisfactory prediction of the ternary data. As shown in Figure 17, the prediction of the distribution curve was fairly good in the dilute pyridine region, indicating that the slopes of the tie-lines corresponded to the experimental data.

Table 18. Experimental Tie-line Data for the System: Benzene (1)--Water (2)--Pyridine (3) at 60° C.

| Tie-line | Alpha Phase Composition | | | Beta Phase Composition | | |
|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | $x_1$ | $x_2$ | $x_3$ |
| 1. | 0.675 | 0.086 | 0.239 | 0.001 | 0.969 | 0.029 |
| 2. | 0.542 | 0.152 | 0.306 | 0.002 | 0.944 | 0.054 |
| 3. | 0.508 | 0.164 | 0.328 | 0.003 | 0.905 | 0.092 |
| 4. | 0.475 | 0.187 | 0.338 | 0.012 | 0.876 | 0.112 |
| 5. | 0.436 | 0.218 | 0.346 | 0.012 | 0.836 | 0.152 |
| 6. | 0.404 | 0.242 | 0.354 | 0.022 | 0.808 | 0.170 |
| 7. | 0.374 | 0.269 | 0.357 | 0.033 | 0.773 | 0.194 |

Table 19. Computed Tie-line Values Using the Margules Model for the System: Benzene (1)--Water (2)--Pyridine (3) at 60° C.

I. Values of the Constants Used

| | | |
|---|---|---|
| $A_{12} = 3.18$ | $A_{13} = 0.049$ | $A_{23} = 0.574$ |
| $A_{21} = 1.95$ | $A_{31} = 0.102$ | $A_{32} = 1.172$ |
| $D_{12} = 6.20$ | $D_{13} = -0.027$ | $D_{23} = 1.455$ |
| $C_1 = 0$ | $C_2 = 0$ | $C_3 = 0$ |
| $q_1 = 1.0$ | $q_2 = 1.0$ | $q_3 = 1.0$ |

II. Computed Tie-lines and Activities

| Tie-line | Alpha Phase Composition<br>Beta Phase Composition | | | Computed Activities in Each Phase | | |
|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | $a_1$ | $a_2$ | $a_3$ |
| 1. | 0.763 | 0.037 | 0.200 | 0.794 | 0.985 | 0.218 |
| | 0.0007 | 0.979 | 0.0203 | 0.800 | 0.982 | 0.222 |
| 2. | 0.706 | 0.044 | 0.250 | 0.748 | 0.984 | 0.265 |
| | 0.0007 | 0.973 | 0.0263 | 0.745 | 0.978 | 0.266 |
| 3. | 0.584 | 0.086 | 0.330 | 0.715 | 0.982 | 0.297 |
| | 0.0008 | 0.908 | 0.091 | 0.709 | 0.980 | 0.285 |

The system: benzene--water--ethanol.--The liquid-liquid equilibria for the ternary system, benzene--water--ethanol was studied by Varteressian and Fenske (48), Bancroft and Hubbard (49), and Barbaudy (50) to name a few of many investigators of this ternary system. The data of Bancroft and Hubbard (49) were used for the comparison of the predicted results against experimental results, since reference (48) apparently contained

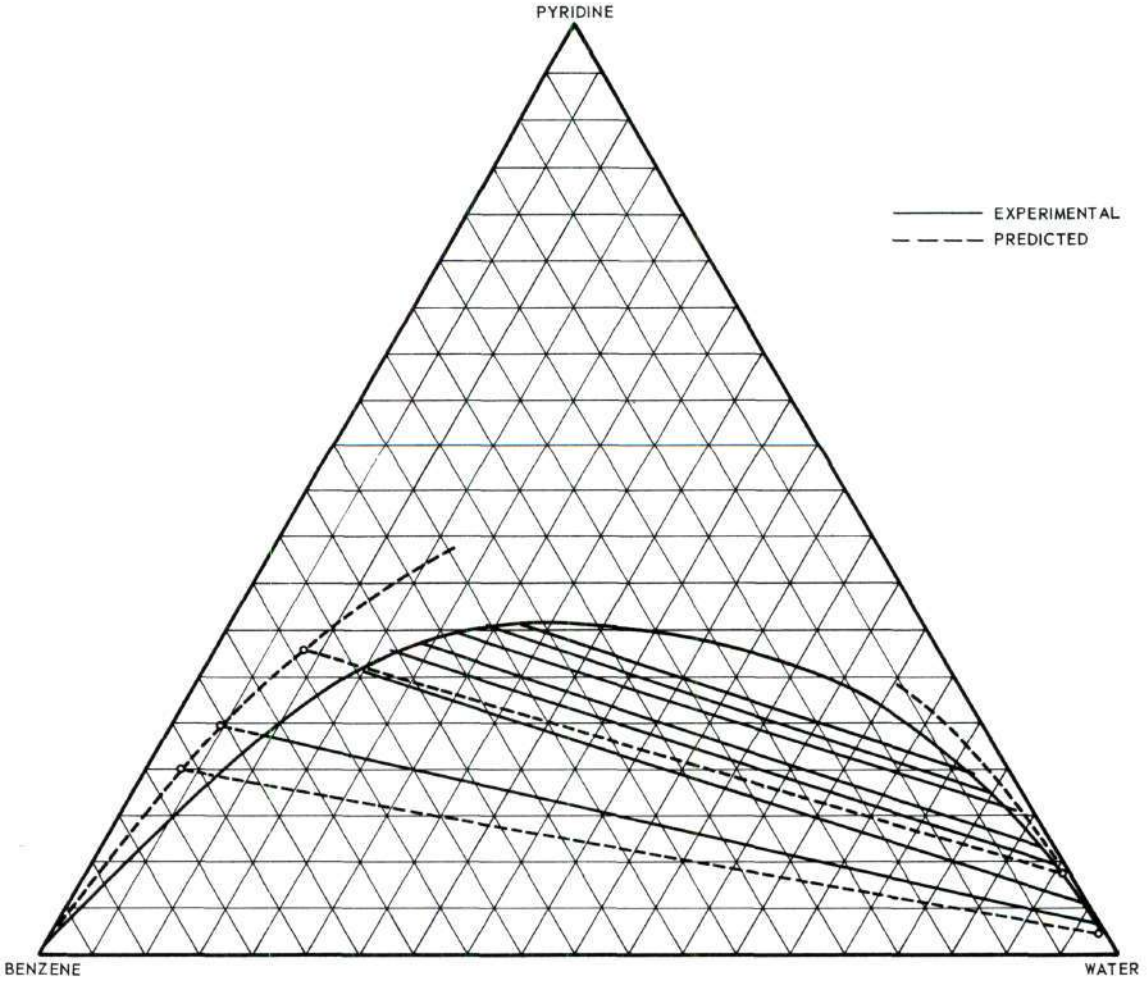


Figure 16. Experimental and computed liquid-liquid equilibrium using the Margules model for the system: benzene--water--pyridine at 60°C.

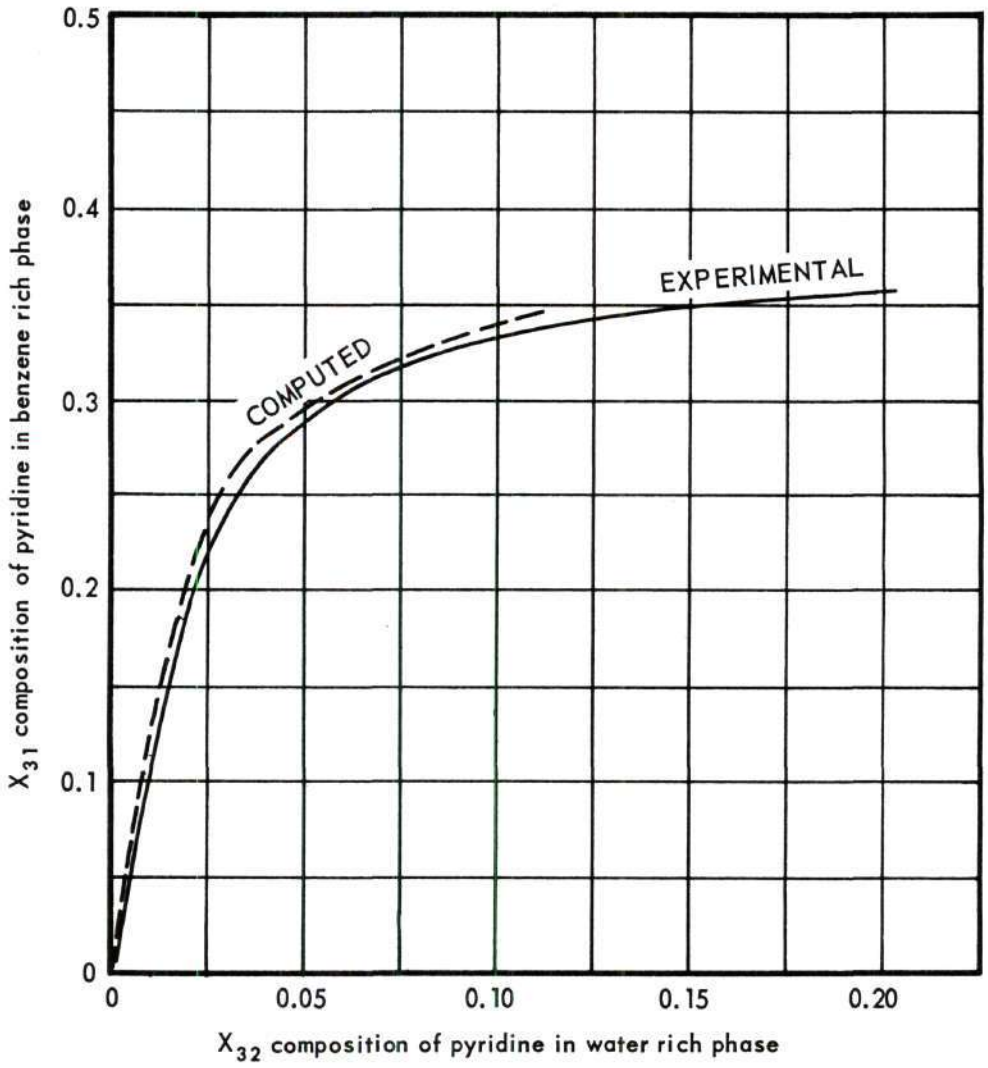


Figure 17. Experimental and computed distribution curves for the system: benzene--water--pyridine at 60°C.

some typographical errors. It was noted, however, that there was considerable disagreement in the literature as to liquid-liquid equilibrium data, and there is some question in this author's mind as to the reliability of the experimental data. The results of the predictions of the tie-lines were poor in the regions of substantial ethanol concentration. For this system, the computed distribution curves agreed with the experimentally determined distribution curves only in the dilute ethanol regions. These results are comparable to those obtained for the system benzene--water--pyridine.

Table 20. Experimental Tie-line Data for the System: Benzene (1)--Water (2)--Ethanol (3) at 25° C.

| Tie-line | Alpha Phase Composition | | | Beta Phase Composition | | |
|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | $x_1$ | $x_2$ | $x_3$ |
| 1. | 0.986 | 0.004 | 0.010 | 0.000 | 0.961 | 0.038 |
| 2. | 0.958 | 0.008 | 0.033 | 0.000 | 0.920 | 0.079 |
| 3. | 0.921 | 0.021 | 0.058 | 0.001 | 0.869 | 0.129 |
| 4. | 0.835 | 0.036 | 0.129 | 0.010 | 0.755 | 0.235 |
| 5. | 0.827 | 0.040 | 0.133 | 0.011 | 0.748 | 0.241 |
| 6. | 0.789 | 0.050 | 0.161 | 0.018 | 0.703 | 0.279 |
| 7. | 0.746 | 0.064 | 0.189 | 0.034 | 0.649 | 0.317 |
| 8. | 0.698 | 0.077 | 0.225 | 0.054 | 0.591 | 0.355 |
| 9. | 0.636 | 0.102 | 0.262 | 0.096 | 0.510 | 0.394 |
| 10. | 0.581 | 0.126 | 0.293 | 0.133 | 0.456 | 0.411 |
| 11. | 0.503 | 0.166 | 0.331 | 0.211 | 0.372 | 0.418 |

Table 21. Computed Tie-line Values Using the Margules Model for the System: Benzene (1)--Water (2)--Ethanol (3) at 25° C.

I. Values of the Constants Used.

| | | |
|---|---|---|
| $A_{12} = 3.40$ | $A_{13} = 0.725$ | $A_{23} = 0.380$ |
| $A_{21} = 2.06$ | $A_{31} = 1.030$ | $A_{32} = 0.695$ |
| $D_{12} = 0.00$ | $D_{13} = 0.340$ | $D_{23} = 0.104$ |
| $C_1 = 0$ | $C_2 = 0$ | $C_3 = 0$ |
| $q_1 = 1.0$ | $q_2 = 1.0$ | $q_3 = 1.0$ |

II. Computed Tie-lines and Activities.

| Tie-line | Alpha Phase Composition<br>Beta Phase Composition | | | Computed Activities in Each Phase | | |
|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | $a_1$ | $a_2$ | $a_3$ |
| 1. | 0.861 | 0.039 | 0.100 | 0.910 | 0.856 | 0.464 |
| | 0.0095 | 0.755 | 0.2355 | 0.907 | 0.860 | 0.446 |
| 2. | 0.838 | 0.042 | 0.120 | 0.904 | 0.845 | 0.495 |
| | 0.017 | 0.670 | 0.313 | 0.907 | 0.837 | 0.479 |
| 3. | 0.816 | 0.044 | 0.140 | 0.899 | 0.815 | 0.518 |
| | 0.034 | 0.557 | 0.409 | 0.899 | 0.812 | 0.505 |
| 4. | 0.793 | 0.047 | 0.160 | 0.895 | 0.803 | 0.533 |
| | 0.0485 | 0.493 | 0.4585 | 0.891 | 0.797 | 0.518 |
| 5. | 0.771 | 0.049 | 0.180 | 0.892 | 0.776 | 0.545 |
| | 0.068 | 0.433 | 0.499 | 0.887 | 0.781 | 0.528 |
| 6. | 0.747 | 0.053 | 0.200 | 0.890 | 0.775 | 0.551 |
| | 0.083 | 0.396 | 0.521 | 0.888 | 0.771 | 0.533 |
| 7. | 0.705 | 0.055 | 0.240 | 0.889 | 0.705 | 0.560 |
| | 0.210 | 0.223 | 0.567 | 0.885 | 0.706 | 0.560 |
| 8. | 0.727 | 0.053 | 0.220 | 0.889 | 0.727 | 0.561 |
| | 0.140 | 0.293 | 0.567 | 0.876 | 0.731 | 0.553 |

Nitromethane--n-heptane--benzene.--The ternary liquid system nitromethane--n-heptane--benzene, was studied by Kimura, et al. (44) at 30° C. and by Francis (45) at 25° C. The latter investigator did not present any tie-line data. The prediction of the ternary equilibrium is compared with the experimental data in Figure 18 using the van Laar model. The prediction is satisfactory in regions dilute in benzene, but becomes poor in the region of the plait point. Similar results were obtained for the Margules model but are not shown here.

Table 22. Experimental Tie-line Data for the System: Nitromethane (1)--n-heptane (2)--Benzene (3) at 30° C.

| Tie-line | Alpha Phase Composition | | | Beta Phase Composition | | |
|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | $x_1$ | $x_2$ | $x_3$ |
| 1. | 0.949 | 0.021 | 0.030 | 0.057 | 0.866 | 0.076 |
| 2. | 0.942 | 0.022 | 0.036 | 0.057 | 0.853 | 0.091 |
| 3. | 0.934 | 0.023 | 0.043 | 0.062 | 0.817 | 0.121 |
| 4. | 0.904 | 0.026 | 0.069 | 0.071 | 0.774 | 0.155 |
| 5. | 0.898 | 0.027 | 0.075 | 0.081 | 0.734 | 0.185 |

Table 23. Computed Tie-line Values Using the van Laar Model for the System: Nitromethane (1)-- n-heptane (3)--Benzene (3) at 30° C.

I. Values of the Constants Used

| | | |
|---|---|---|
| $A_{12} = 1.451$ | $A_{13} = 0.556$ | $A_{23} = 0.241$ |
| $A_{21} = 1.743$ | $A_{31} = 0.535$ | $A_{32} = 0.127$ |
| $D_{12} = 0$ | $D_{13} = 0$ | $D_{23} = 0$ |
| $C_1 = 0$ | $C_2 = 0$ | $C_3 = 0$ |

II. Computed Tie-lines and Activities.

| Tie-line | Alpha Phase Composition<br>Beta Phase Composition | | | Computed Activities in Each Phase | | |
|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | $a_1$ | $a_2$ | $a_3$ |
| 1. | 0.915 | 0.025 | 0.060 | 0.929 | 0.823 | 0.166 |
| | 0.062 | 0.788 | 0.150 | 0.932 | 0.821 | 0.172 |
| 2. | 0.817 | 0.033 | 0.150 | 0.865 | 0.678 | 0.338 |
| | 0.094 | 0.596 | 0.310 | 0.873 | 0.685 | 0.339 |
| 3. | 0.736 | 0.044 | 0.220 | 0.827 | 0.618 | 0.425 |
| | 0.118 | 0.492 | 0.390 | 0.831 | 0.618 | 0.418 |
| 4. | 0.665 | 0.055 | 0.280 | 0.801 | 0.564 | 0.478 |
| | 0.150 | 0.398 | 0.452 | 0.804 | 0.563 | 0.479 |
| 5. | 0.575 | 0.075 | 0.350 | 0.780 | 0.552 | 0.521 |
| | 0.180 | 0.328 | 0.492 | 0.779 | 0.521 | 0.521 |
| 6. | 0.500 | 0.100 | 0.400 | 0.774 | 0.508 | 0.538 |
| | 0.200 | 0.296 | 0.504 | 0.774 | 0.505 | 0.535 |

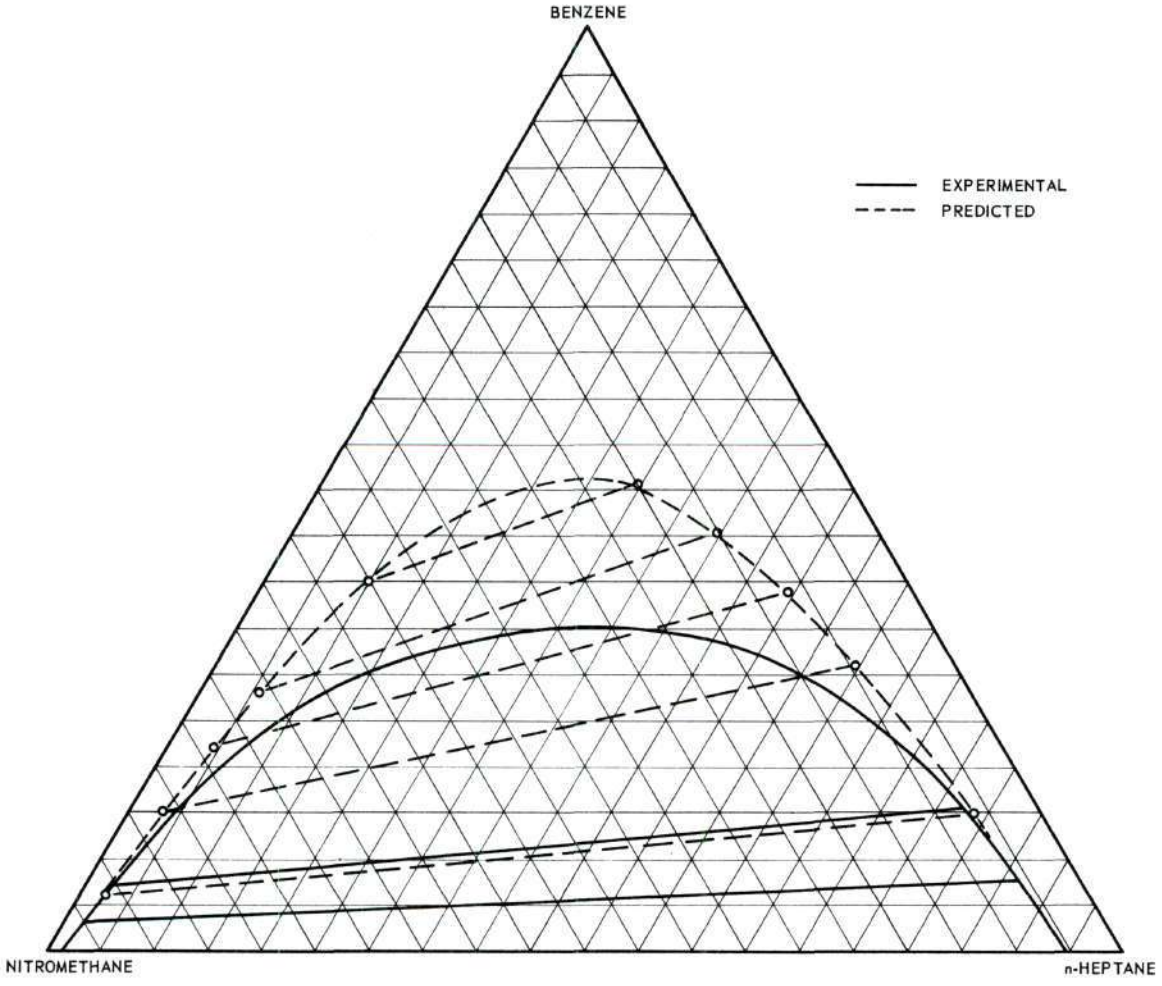


Figure 18. Experimental and computed liquid-liquid equilibrium using the van Laar model for the system: nitromethane--n-heptane--benzene at 30°C.

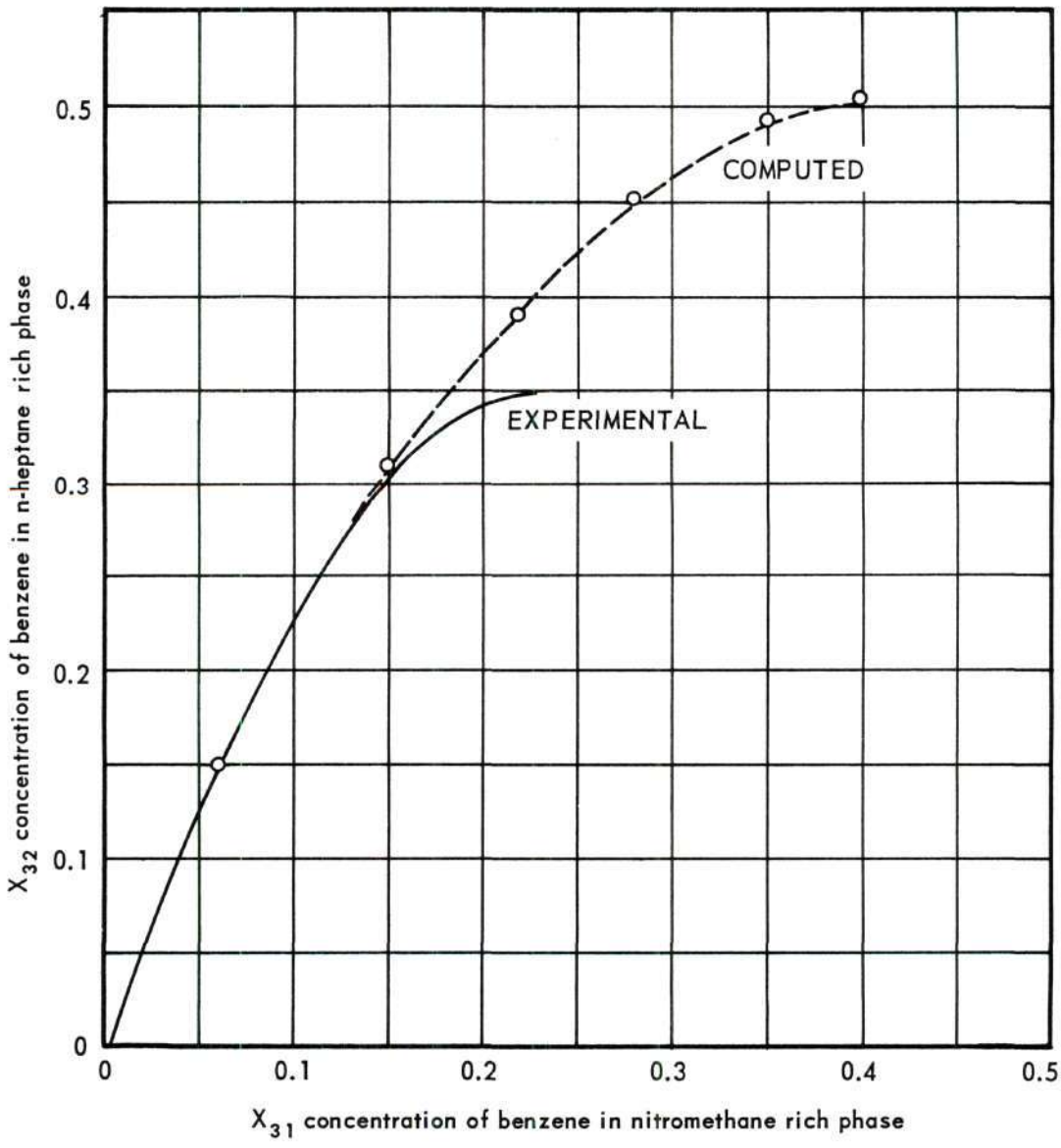


Figure 19. Experimental and computed distribution curves for the system: nitromethane--n-heptane--benzene at 30°C.

The system: decyl alcohol--nitromethane--ethylene glycol.--The ternary system, decyl alcohol--nitromethane--ethylene glycol, consisting of three separate binodal curves was studied by Francis (51) at various temperatures. Vapor-liquid equilibrium were not available for any of the component binary systems. Since each of the binary mixtures were partially miscible, the parameters to the two-constant standard equations were computed from the mutual solubility at 26° C. and are given in Appendix D.

This phase of the investigation was undertaken to ascertain whether a ternary empirical model was capable of predicting a free energy surface of such complexity as exists in a system composed of three binodal curves. As can be seen from the experimental data in Figure 20, the binodal curves are not symmetric and are of different sizes. The computations are summarized in Table 24. The results indicate that a model is capable of predicting three binodal curves, although the prediction in this case was very poor. Some difficulty was encountered in the region rich in nitromethane where two of the binodal curves come close together. The calculations almost indicate an overlapping of binodal curves, a situation which is physically impossible.

Table 24. Computed Tie-line Values Using the van Laar Model for the System: Decyl Alcohol (1)--Nitromethane (2)--Ethylene Glycol (3) at 26° C.

I. Values of the Constants Used.

| | | |
|---|---|---|
| $A_{12} = 1.696$ | $A_{13} = 1.667$ | $A_{23} = 0.788$ |
| $A_{21} = 0.914$ | $A_{31} = 0.397$ | $A_{32} = 1.308$ |
| $D_{12} = 0$ | $D_{13} = 0$ | $D_{23} = 0$ |
| $C_1 = 0$ | $C_2 = 0$ | $C_3 = 0$ |

II. Computed Tie-lines and Activities.

| Tie-line | Alpha Phase Composition<br>Beta Phase Composition | | | Computed Activities in Each Phase | | |
|---|---|---|---|---|---|---|
| | $x_1$ | $x_2$ | $x_3$ | $a_1$ | $a_2$ | $a_3$ |
| 1. | 0.751 | 0.199 | 0.050 | 0.791 | 0.976 | 0.108 |
| | 0.023 | 0.970 | 0.007 | 0.788 | 0.974 | 0.111 |
| 2. | 0.682 | 0.218 | 0.100 | 0.726 | 0.967 | 0.209 |
| | 0.021 | 0.966 | 0.013 | 0.734 | 0.969 | 0.206 |
| 3. | 0.596 | 0.254 | 0.150 | 0.653 | 0.966 | 0.303 |
| | 0.019 | 0.962 | 0.019 | 0.651 | 0.965 | 0.304 |
| 4. | 0.461 | 0.339 | 0.200 | 0.614 | 0.967 | 0.356 |
| | 0.017 | 0.958 | 0.025 | 0.607 | 0.962 | 0.368 |
| 5. | 0.269 | 0.511 | 0.220 | 0.584 | 0.961 | 0.376 |
| | 0.014 | 0.955 | 0.031 | 0.578 | 0.957 | 0.388 |
| *6. | 0.286 | 0.363 | 0.351 | 0.474 | 0.864 | 0.652 |
| | 0.012 | 0.936 | 0.052 | 0.486 | 0.867 | 0.643 |
| *7. | 0.016 | 0.010 | 0.974 | 0.643 | 0.486 | 0.746 |
| | 0.378 | 0.043 | 0.579 | 0.636 | 0.477 | 0.739 |

*Belongs to second and third phases.

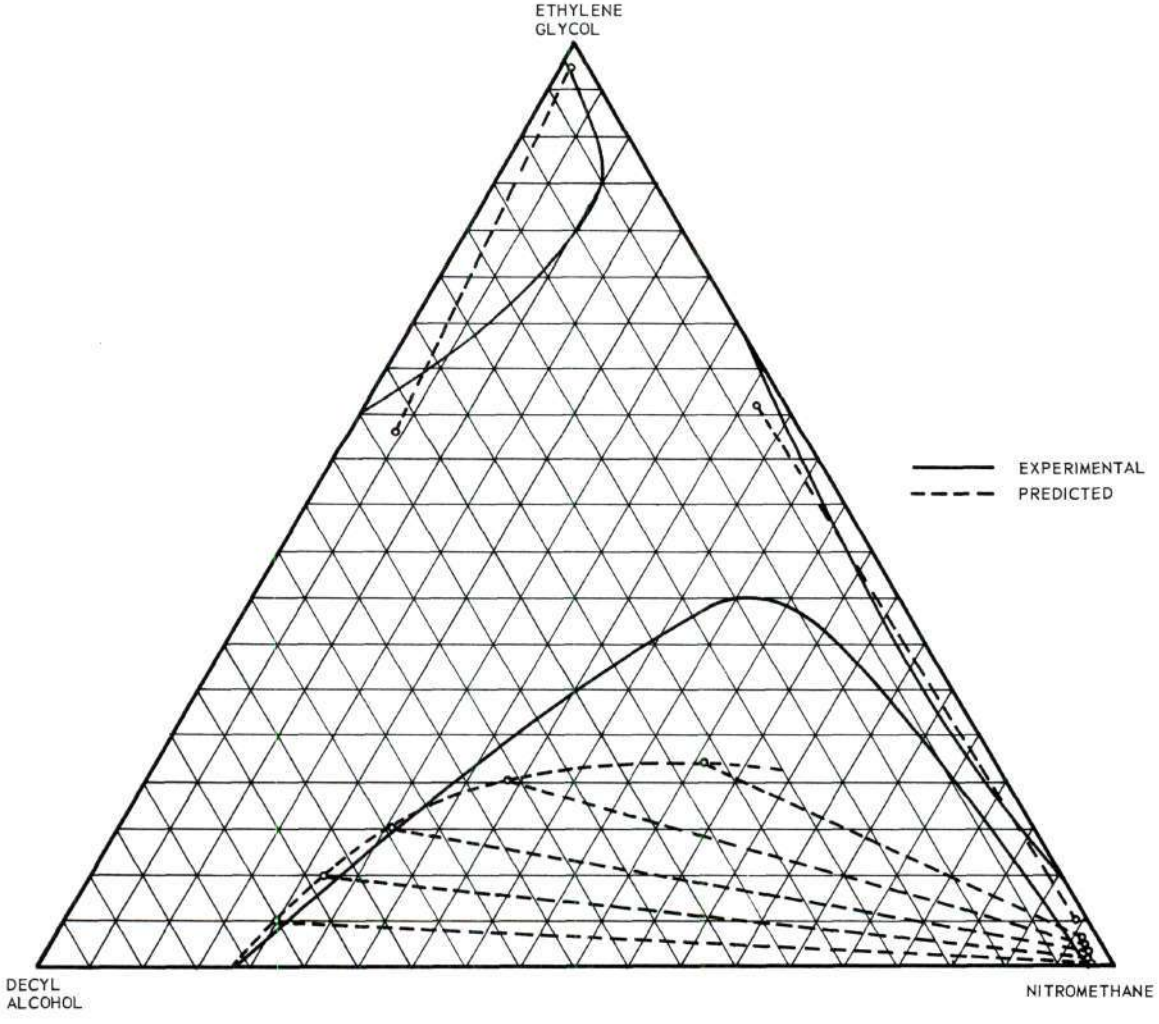


Figure 20. Experimental and computed liquid-liquid equilibrium using the van Laar model for the system: decyl alcohol--nitromethane--ethylene glycol at 26°C.

# PART II. THE TREATMENT OF BINARY VAPOR-LIQUID EQUILIBRIUM DATA

It is the purpose of this part to present a technique for the treatment of binary vapor-liquid equilibrium data using digital computing equipment. The objectives of this treatment will be to provide some mathematical functions, specifically polynomials, which will represent the experimental data in the best possible manner, and secondly to provide a precise method for determining the validity of the data. The meaning of the phrase "...the validity of the data," in terms of thermodynamic consistency will be discussed in Chapter V. The technique and the relations involved in obtaining a mathematical representation of the data will also be developed in this chapter. The application to thermodynamic consistency will be presented along with a discussion of what is meant by obtaining the best representation of experimental data. Chapter VI will conclude this part with a discussion of some of the results of using this technique on specific binary systems. The computations for the binary system, ethanol-benzene are presented in detail in Appendix C to demonstrate the technique.

# CHAPTER V

## THERMODYNAMIC CONSISTENCY OF VAPOR-LIQUID EQUILIBRIUM DATA

Once experimental vapor-liquid data are obtained, it is desirable that some means of examining the validity of the observed data be employed. Equilibrium measurements are always subject to errors depending on the apparatus and the accuracy of the measurements. If the data are graphically depicted, large random errors are easily found as they usually show up as deviations from a smooth curve. The majority of the data presented in the literature have already been smoothed and these random errors have been eliminated. It has been pointed out (52) that the random errors are especially apparent on a plot showing the difference of the mole fractions in the vapor and liquid phase (y-x) versus the composition of the liquid (x).

The smoothness of the curve, however, is not a guarantee of the reliability of the data, since the experiment can be conducted in such a manner as to introduce a systematic error which does not show up as a scattering of the measured points. These systematic errors are usually caused by improper functioning of the equipment. Only by comparison with some thermodynamically exact relations, can the consistency of measured data be checked. The Gibbs-Duhem equation (equation (8)) being a necessary and sufficient relation between the partial molar properties of the components in a mixture, is generally used to test the experimental measurements for thermodynamic consistency. This test is applied in several

different ways depending upon the variation in the Gibbs-Duhem equation used.

The test of thermodynamic consistency favored by many authors appears to be a graphical integration of the difference of the excess chemical potentials or activity coefficients (53), (54). The use of graphical integration can lead to serious errors if the investigator is not careful. The values of the integrand become indeterminate in the dilute region and may fluctuate enough to significantly affect the value of the integral. Another aspect to the use of the area test, as this method is commonly called, is to represent each of the excess chemical potentials by some functions of the liquid compositions. One may then evaluate the integral and find it to be zero and yet the Gibbs-Duhem equation is not satisfied. The reason for this can easily be seen if the excess free energy function is determined; then computing the partial devivative with respect to one of the moles will not give back the original excess chemical potential function. This occurs when one fits each of the excess chemical potentials with a polynomial of different degree. Thus the area test is only a necessary condition for thermodynamic consistency but the Gibbs-Duhem equation is both necessary and sufficient. The main difficulty in the use of these relations is in the accuracy with which one can compute the partial molal quantities.

There are many instances where the conditions of the equilibrium experiment have been ignored in testing the data for thermodynamic consistency. Equation (8) is very often used without any justification even though it is impossible to conduct a vapor-liquid equilibrium experiment under both isothermal and isobaric conditions simultaneously. Examination

of equation (7) shows the terms which are neglected.

If one considers a vapor-liquid equilibrium experiment to be carried out under isobaric conditions then equation (66) would be the relation required for the determination of the consistency of the data.

$$x_1 \left(\frac{\partial \mu_1^E}{\partial x_1}\right)_p + x_2 \left(\frac{\partial \mu_2^E}{\partial x_1}\right)_p + \frac{\Delta H^m}{T} \left(\frac{dT}{dx_1}\right)_p = 0 \qquad (66)$$

As seen from equation (66), heat of mixing data would be required in conjunction with isobaric vapor-liquid equilibrium data if the latter data were to be tested for thermodynamic consistency. The contribution of the term containing the heat of mixing has been shown to be significant when compared to the other terms (55) and thus cannot be neglected.

With regard to the examination of the validity of binary isobaric vapor-liquid equilibrium data for the systems considered in this work, it was decided to recommend this as an area for further study inasmuch as heat of mixing data were not readily available for these particular binary systems. Thus binary isobaric data were not examined for thermodynamic consistency.

The Gibbs-Duhem equation for an isothermal binary system can be written as follows,

$$x_1 \left(\frac{\partial \mu_1^E}{\partial x_1}\right)_T + x_2 \left(\frac{\partial \mu_2^E}{\partial x_1}\right)_T - \Delta v^m \left(\frac{dp}{dx_1}\right)_T = 0 \qquad (67)$$

For the pressure and temperature ranges of the systems studied, the volume term, $\Delta v^m dp/dx$, is small when compared to the other terms of equation (67) and can usually be neglected (56). This is not true for systems

where the excess free energy of the mixture is small and thus the magnitude of the volume term becomes comparable to the other terms. For non-ideal miscible binary systems, exhibiting azeotropes and where the excess free energy is large, the volume term is negligible. Appendix C discusses the contribution of this term for the system, ethanol--benzene at 45° C. For subsequent discussions of the treatment of binary systems, which are considered in this work, the volume term will be neglected. Equation (68) represents the form of the Gibbs-Duhem equation for a binary system under isothermal conditions which will be used in this discussion.

$$x_1 \left(\frac{\partial \mu_1^E}{\partial x_1}\right)_T + x_2 \left(\frac{\partial \mu_1^E}{\partial x_1}\right)_T = 0 \qquad (68)$$

Equations (69), (70), and (71) are this author's representation of the Gibbs-Duhem equation in terms of the experimentally determined quantities. Equations (69) and (70) are obtained by partial differentiation of equations (31) and (32) with respect to the mole fraction of component one of a binary system holding the temperature to be constant.

$$x_1 \left(\frac{\partial \mu_1^E}{\partial x_1}\right)_T = \left(\frac{RTx_1}{P} + (B_{11} - v_1^o)x_1 + R_{12}y_2^2 x_1\right)\left(\frac{dP}{dx_1}\right) + \left(\frac{RTx_1}{y_1} - 2R_{12}Py_2x_1\right)\frac{dy_1}{dx_1} - RT \qquad (69)$$

$$x_2 \left(\frac{\partial \mu_2^E}{\partial x_1}\right)_T = \left(\frac{RTx_2}{P} + (B_{22} - v_2^o)x_2 + R_{12}y_1^2 x_2\right)\left(\frac{dP}{dx_1}\right) + \left(2R_{12}Py_1x_2 - \frac{RTx_2}{y_2}\frac{dy_1}{dx_1}\right) + RT \qquad (70)$$

Substitution of equations (69) and (70) into equation (68) gives,

$$\left(\frac{RT}{P} + (B_{11} - v_1^{\circ})x_1 + (B_{22} - v_2^{\circ})x_2 + R_{12}(y_2^2 x_1 + y_1^2 x_2)\right)\frac{dP}{dy_1} + \left(RT\left(\frac{x_1 - y_1}{y_1 y_2}\right) + 2R_{12}P(y_1 - x_1)\right) = 0 \quad (71)$$

Equation (71) is the same as an equation derived by Scatchard (57) but in a different form, viz.,

$$\frac{y_1 - x_1}{y_1 y_2} = (1 + D)\frac{d \ln P}{dy} \quad (72)$$

where

$$D = \frac{\frac{P}{RT}\left[x_1(B_{11} - v_1^{\circ}) + x_2(B_{22} - v_2^{\circ}) + R_{12}(x_1 y_2^2 - x_2 y_1^2 + 2y_1 y_2)\right]}{1 - \frac{P}{RT}\,2R_{12}y_1 y_2} \quad (73)$$

Equation (71) will form the basis for all computations of isothermal binary systems. The method of using equation (71) will now be developed.

Mathematical representation of binary vapor-liquid equilibrium data.-- It is the purpose of this section to present a technique for the characterization of binary equilibrium data using digital computers. It is hoped that this can be a standard process for all equilibrium measurements, inasmuch as human bias would be eliminated. Since experimental data yield a set of discrete points usually unequally spaced, with each measurement having some error associated with it, the problem to be solved is how these data can best be described in a mathematical sense. Jost and Roeck (58) have implied that by the use of Vettin's discontinuous orthogonal

polynomials the problem stated is solved, but this is not really so, for their method requires equally spaced equilibrium measurements. Obtaining equally spaced equilibrium measurements is a very difficult procedure. The method presented in this section uses orthogonal polynomials for which unequally spaced data points can be used.

The application of orthogonal polynomials to the general problem of fitting experimental data is certainly not new. It is the objective of this immediate discussion to describe a method for the application of orthogonal polynomials to the treatment of isothermal vapor-liquid equilibrium data and to bring in the concept of thermodynamic consistency to find the best degree of fitting polynomials to use on a given set of data.

The most difficult part of the problem is to derive a scheme for the adequate functional representation of a discrete set of data points subject to experimental error. In a sense, the upper bound on the error should at least duplicate the results obtained by a graphical plotting procedure.

Let $(x_i, f_i)$ $i = 1, \ldots, m$ be a set of m pairs of real numbers, where $f_i$ is an experimental observation corresponding to the value $x_i$. The problem is to find, among all polynomials of degree k, that polynomial which best fits the set of points $(x_i, f_i)$ in some prescribed sense.

$$y_k(x) = P_o^{(k)} + P_1^{(k)} x + \ldots + P_k^{(k)} x^k \qquad (74)$$

The sense prescribed here will be roughly that $y_k(x_i) - f_i$ is small for each $i = 1, \ldots, m$, and there are many ways to accomplish this.

For a graphical depiction one makes the statement that fitting the data means drawing a smooth curve through the data points. Examining this

statement in detail, one immediately notices a contradiction, in that, since the data are subject to experimental errors due to vagaries of the measuring instruments, etc., it might not be possible to construct a smooth curve through the data points. In such cases, one uses a curve which is best by some definition to be discussed below. And secondly, since one does not have geometric points, the phrase "through the points" would simply mean that the difference $y_k(x_i) - f_i$ is less than the thickness of the drawing instrument one is using, but most certainly not equal to zero. Thus there is hope that a graphical procedure can be duplicated on the computer.

If the degree of the polynomial is greater than the number of points, then the parameters, $P_i$, would be selected in such a manner as to make the polynomial $y_k(x)$ pass through each point $(x_i, f_i)$. However, the usual problem is one in which the degree of the polynomial is less than the number of points, resulting in the fact that the $y_k(x_i) - f_i$ cannot all be made zero simultaneously.

If one defines the m numbers, $e_i = y_k(x)_i - f_i$, to be the m components of an error vector, then the problem of best fitting a curve corresponds to the selection of a norm $||e||$ for the vector e. A most commonly used norm in these cases is the Euclidean norm

$$||e|| = (e_1^2 + e_2^2 + \ldots + e_m^2)^{1/2} \qquad (75)$$

since it is usually assumed that the observed values, $f_i$, are subject to independent normally distributed errors about their trend, and hence the use of this norm is demanded by regression theory (59). The precise formulation of our problem is that of finding values of the parameters $P_o^{(k)}$,

$P_1^{(k)}, \ldots, P_k^{(k)}$ so that

$$\| e \| = \text{minimum.} \tag{76}$$

In a least squares fitting problem where a polynomial is being fitted to a set of data points, the resulting set of linear equations, called normal equations, gives good results for varying degrees of polynomials up to 5 or 6.

When the degree of the fitting polynomial, k, is greater than 7 or 8, Forsythe (59) has shown that the coefficient matrix of the normal equations roughly approximates something like m times the principal minor of order k + 1 of the infinite Hilbert matrix, H. Furthermore, it has been observed that systems of linear equations involving minors of H are very difficult to solve. For k = 9, for example, the order of the principal minor $H_{10}$ is 10 and the inverse $H_{10}^{-1}$ has elements of magnitude $3 \times 10^{12}$. Thus a slight error of $10^{-10}$ in the constant term of the coefficient matrix will lead to errors of approximately 300 in the $P_i^{(k)}$ corresponding to the solution of the normal equations.

In using orthogonal polynomials to best fit the data values $f_i$, the following form is used:

$$y_k(x) = c_o^{(k)} t_o(x) + c_1^{(k)} t_1(x) + \ldots + c_k^{(k)} t_k(x) \tag{77}$$

The development of the normal equations follows the usual procedure,

$$V(c_o^{(k)}, c_1^{(k)}, \ldots, c_k^{(k)}) = \sum_{i=1}^{m} (f_i - \sum_{j=0}^{k} c_j^{(k)} t_j(x_i))^2 =$$

$$\text{minimum} \tag{78}$$

Introducing the following abbreviations:

$$a_{hj} = \sum_{i=1}^{m} t_h(x_i)t_j(x_i) \qquad b_h = \sum_{i=1}^{m} f_i t_h(x_i) \tag{79}$$

we write the set of normal equations

$$\begin{aligned} a_{oo}c_o^{(k)} + \ldots + a_{ok}c_k^{(k)} &= b_o \\ a_{ko}c_o^{(k)} + \ldots + a_{kk}c_k^{(k)} &= b_k \end{aligned} \tag{80}$$

which determine the $c_i^{(k)}$ uniquely provided the matrix of coefficients $(a_{ik})$ is nonsingular. Now for the set of normal equations to be easily solvable for large values of k, it is sufficient to make the diagonal elements $a_{ii}$ much larger than the off-diagonal elements $a_{ij}(i \neq j)$. There are many methods for accomplishing this.

The method which we shall use is to have our polynomials $t_i(x)$ orthogonal over the point set $x_i, \ldots x_m$ according to the development by Forsythe (59).

$$a_{nj} = \sum_{i=1}^{m} t_n(x_i)\, t_j(x_i) = 0 \quad h \neq j \tag{81}$$

This equation, when used in conjunction with (78), gives a set of normal equations of the following simple form:

$$\begin{aligned} a_{oo}c_o^{(k)} &= b_o \\ a_{ll}c_l^{(k)} &= b_l \\ \ldots\ldots & \ldots \\ a_{kk}c_k^{(k)} &= b_k \end{aligned} \tag{82}$$

Thus we see that the coefficient $c_i^{(k)}$ depends only on i and the number of points used, but not on the degree k. Furthermore, the normal equations are very easy to solve.

The orthogonal polynomials are generated by the following relations:

$$t_o(x) = 1 \tag{83a}$$

$$t_1(x) = x\, t_o(x) - \alpha_1 t_o(x) \tag{83b}$$

$$t_2(x) = (x - \alpha_2)\, t_1(x) - \beta_1 t_o(x) \tag{83c}$$

$$t_{i+1}(x) = (x - \alpha_{i+1})\, t_i(x) - \beta_i t_{i-1}(x) \tag{83}$$

where $\alpha_i$ and $\beta_i$ are numbers chosen to make the orthogonality relations hold.

Briefly the following scheme as outlined in reference (59) is used:

1. Compute $b_i = (f, t^{(i)})$
2. Compute $c_i = b_i/a_{ii}$ $\quad (a_{oo} = m)$
3. Compute $\alpha_{i+1} = (x, t_i)^2/a_{ii}$
4. Compute Vector $t_{i+1} = (x - \alpha_{i+1})\, t_i - \beta_i t_{i-1}$ $\quad (\beta_o = 0)$
5. Compute $a_{i+1,i+1} = (t_{i+1}, t_{i+1})$
6. Increase i to i + 1
7. Compute $\beta_i = a_{ii}/a_{i-1,\,i-1}$
8. Go to step 1.

This gives values of $c_o$, $c_1$, ..., $\alpha_1$, $\alpha_2$, ..., $\beta_1$, $\beta_2$ ... which now permit us to compute the coefficients of the fitting polynomial in x.

$$y_k(x) = \sum_{i=0}^{k} P_i x^i \tag{84}$$

where

$$P_i = \sum_{i=j}^{k} c_i q_{ij}$$

where

$$q_{i+1,j} = \begin{cases} q_{i,j-1} - \alpha_{i+1} q_{ij} - \beta_i q_{i-1,j} \\ 1 \\ 0 \end{cases} \quad \text{for} \quad \begin{cases} i + 1 > j \\ i + 1 = j \\ i + 1 < j \text{ or } j < 0 \end{cases}$$

At this stage a choice can be made as to whether to compute the predicted values from the polynomial approximation given by equation (74), or from the values of the computed parameters $c_o$, $c_1$, ..., $\alpha_1$, $\alpha_2$, ..., $\beta_1$, $\beta_2$, ... in the set of recursive relations given by equation (83). While to an engineer, the polynomial form may be more aesthetic, this author's experience has forced him to concur with Forsythe in the use of the latter technique. If one uses single precision floating point arithmetic (eight significant digits with two digits for an exponent), it has been found that round-off error reduced the number of significant digits to one or less, when a high degree of the polynomial form given by equation (74) was used. As the degree of the polynomial increases, the parameters $P_i$, get extremely large with a net effect of loss of significant figures.

In this treatment of binary vapor-liquid equilibrium data, two separate polynomial fits are obtained which are given by sets of values of $c_0$, $c_1$, ..., $\alpha_1$, $\alpha_2$, ... $\beta_1$, $\beta_2$, ... First the vapor compositions are fitted in terms of liquid compositions and then the total pressures are fitted in terms of the liquid compositions. In both sets of data, the values of the abscissas are the same and hence the values of the $\alpha$'s and $\beta$'s will be the same since they are only functions of the independent variables. Since this method affords the use of high degrees of polynomials, the experimental data can be fitted as close as one desires. Thus one can generate as many interpolated values of the data as is desired. In an isothermal equilibrium experiment, the experimental data are (1) the total pressure on the system, P, and (2) the composition of the vapor, y, both determined at specific liquid compositions.

The currently used technique is to compute the excess chemical potentials (or activity coefficients) directly from the experimental data in terms of the liquid compositions. These values are then fitted by some polynomial or used in an area test for thermodynamic consistency. The major difficulty with this technique is that the end values of the excess chemical potentials are indeterminate.

The proposed method differs from the currently used technique in that the experimental data are fitted by the orthogonal polynomials which are used to generate many interpolated values of pseudo-experimental points. It is these interpolated values which are used to compute the excess chemical potentials. The advantages of this method are as follows:

1. It makes use of the impartial and standard techniques of least squares and orthogonal polynomials for fitting of data with functions of a very general class whose convergence in norm to the required function is assured by Weierstrass' approximation theorem.
2. This method circumvents the problem of the indeterminacy of the excess chemical potential functions at the end points.
3. This method makes use of the necessary and sufficient criterion for thermodynamic consistency, as will be shown below, while the currently used technique uses the necessary condition.
4. There is a liberalization of data points (by the pseudo-experimental points) in order to make various tests possible.
5. There is a minimization of computational error by the use of orthogonal polynomials without any loss of applicability of method.
6. The use of orthogonal polynomials for fitting the data by higher degree polynomials requires only the computation of the coefficients of the highest degree terms.

On functional approximations of experimental data.--In the analysis of experimental data, there are several questions which should be resolved. The term "experimental data" will denote a recorded observation of some physical phenomenon under specified and controlled conditions. If the experiment is to be repeated with the same specified conditions, then it becomes apparent that the previous observations will only be reproducible within some specified range of measurement. This is then called the experimental error. Now, the analysis of experimental data requires a mathematical

study of the totality of these measurements which are thought to be a description of the real physical system under consideration. How then can this real system be best described in a mathematical sense? This question can be broken down to the following questions: How accurate are the measurements when judged from the experimental data themselves? Does a functional relation appear to exist between the variables? If the data appear to be functionally related, then what representations would be the best to use according to a yet-to-be specified criterion? How arbitrary can the fitting equation be and still give rise to like data? Can the fitting equation be used to predict future values, and with what degree of assurance?

Any successful numerical analysis of data demands a careful choice of the underlying mathematical model. If the data are forced into a model which is too simplified, the results obtained are meaningless; if the model is sufficiently descriptive to represent exactly the bounds of the experimental parameters, it often becomes too cumbersome to yield any information. Ideally it is desirable that the mathematical model contain fundamental bases that are deducible from certain basic universal laws. However, it is all too often that the fundamental laws are bound tightly in an insoluble equation, or they are not mathematically representable. In order to circumvent this lack of a fundamental understanding, empirical models are offered as panaceas for many engineering problems. It must be realized that as long as this lack of knowledge exists, empirical models are better than nothing at all.

In this research concerning the effects produced by the intermixing of two or more molecular species in different states of aggregation, it

would be well to note that the fundamental physical laws are, as yet, not completely understood. Hence all postulated models concerning this research are concerned with the characterization of the state of the system rather than with the extrapolation of the states of systems of different molecular species. The best that our empirical model can hope to accomplish would be to say that a type of molecular interaction producing a certain effect in the characterization of the data would manifest itself wherever this type of molecular interaction was present--independent of molecular species. The true answer to the problem lies in the fundamental study of the forces of the molecules.

With this discussion in mind we shall now examine the question of analysis of the data of a particular type of an experiment. The experiment is a study of the equilibrium relationships between the composition of a vapor in contact with a liquid at some observed temperature and pressure for a mixture of two molecular species. It often occurs that data which are utterly worthless get published in the literature. This is because, as yet, there is no precise method of evaluating the data.

The problem of data analysis will now be examined in the specific case of the data of Scatchard and Raymond (57). An equilibrium experiment was conducted at a reported temperature of 54.97° C. (60) on the system ethanol--chloroform. By techniques previously discussed, both the vapor compositions and total pressures, given in terms of liquid compositions for twenty-eight data points were fitted by orthogonal polynomials of degrees two through 23. It was observed that as the degree of the polynomials increased, the sums of the squares of the residuals decreased. Initially it was (perhaps naively) decided to use as the criterion for

ascertaining the degree of the best fitting polynomial, the case where the lowest degree polynomial could be generated such that the residuals at each observed datum would be approximately within the estimated experimental tolerances. Thus the total pressure data were fitted by a polynomial of degree twenty with the sums of squares of residuals equal to 0.95 and no residual greater than 0.55 mm. Hg. The vapor composition data were fitted by a polynomial of degree twenty-two, with a sums of squares of residuals equal to 0.00000088 and the maximum residual being 0.00057.

Subsequent computations with these fitting polynomials involving the use of the excess chemical potentials in the Gibbs-Duhem equation gave very poor results in terms of thermodynamic consistency. Intuitively, it was felt that something was not right, for this study was reported in considerable detail as to reproducibility of results, the nature of the temperature control, purity of substance used, etc.

At this point it should, perhaps, be noted that the following statement concerning the conduct of the experiment was made by the experimentors (61):

> ...the temperature may be reproduced to 0.001° and the pressure may be measured to 0.01 mm. Hg. In favorable cases the compositions of the liquids in the inner boiler and in the condensate trap may be determined to less than 0.1%. However, the equilibrium compositions, temperature and pressure can certainly not be determined to this order of accuracy. Only a careful study of several systems can show how accurately the equilibrium properties may be determined by this method.

The following quotation is also pertinent to the study of this particular system: "Fluctuations in the pressure due to the boiling were not greater than 0.02 mm." (57).

Examination of the various total pressure data polynomial fits revealed that for degrees less than seventeen the maximum of the residuals

was greater than one millimeter of mercury. This would indicate that the total pressure data were not smooth. In the case of equilibrium experiments, the total pressure measurement is indeed very prone to errors, inasmuch as it is greatly affected by the slightest change in temperature for this system. It was noted that the pressure differential over the entire composition range was approximately 400 mm. Hg.

The vapor composition data, on the other hand, graphically displayed no anomalies. Fits of the vapor composition data yielded values of the sums of squares of residuals which decreased very slowly for degrees six and higher of the fitting polynomials. Thus it was felt that the fit of the total pressure data was more sensitive to the further computations that were made.

Hence, it was decided to re-examine the entire question of ascertaining a criterion for a polynomial fit with regard to published experimental data. A plot of experimental total pressure observations immediately revealed what might be called deviations from smooth data. Another way of stating this would be to say that it was observed that the data were not representable by a function whose first derivative would change gradually. These viewpoints are based on the fact that the fitting function should minimize the residuals to within the prescribed experimental error of 0.02 mm. Hg.

Therefore, the question naturally arises as to whether the observed pressures are correct to within prescribed tolerances or whether some gross errors exist. With published data, misprints, unfortunately, must be included in the category of gross errors. A careful review of the paper (57) revealed that one of the observed pressures was actually a misprint.

Table 25. A Comparison of the Sums of Squares of Residuals for the Total Pressure Data Containing a Misprint Against the Observed Data.

| Polynomial Degree | Corrected Data | Uncorrected Data |
|---|---|---|
| 2 | 705 | 681 |
| 3 | 467 | 499 |
| 4 | 463 | 492 |
| 5 | 28 | 75 |
| 6 | 27 | 70 |
| 7 | 9 | 67 |
| 8 | 7 | 65 |
| 9 | 6.7 | 50 |
| 10 | 5.0 | 47 |
| 11 | 5.0 | 37 |
| 12 | 4.5 | 26 |
| 13 | 4.5 | 20 |
| 14 | 3.4 | 8.8 |
| 15 | 3.2 | 5.8 |
| 16 | 3.2 | 4.4 |
| 17 | 2.9 | 3.1 |
| 18 | 2.8 | 2.8 |
| 19 | 2.2 | 2.2 |
| 20 | 0.95 | 0.95 |
| 21 | 1.08* | 1.08* |
| 22 | 19.7* | 19.7* |

*round-off error

After correcting this error in the published data, a new set of fitting polynomials was computed. The new polynomial fits were substantially improved. That is to say, the sums of squares of residuals of the polynomial fits decreased more rapidly in the new case than with the old case (see Table 25). From an examination of the different degrees of polynomial fits there was one point which consistently had a residual greater than one millimeter of mercury. The reconciliation of this datum poses some questions of a fundamental nature.

Those concerned with the conduct of the experiment can perhaps readily justify the exclusion of this wandering datum in terms of self-criticism. There is no doubt that, indeed much of the published experimental data has been smoothed by either rejecting the outlying data points or moving them into line.

From the viewpoint of one who is completely detached from the experiment, but who is charged with the responsibility of evaluating the data, in this case for thermodynamic consistency, the question of experimental integrity becomes exceedingly difficult to answer. Through a posteriori knowledge it must be assumed that the real physical world is describable by smooth continuous functions except at known singular regions. In this work a smooth continuous function is by definition a polynomial of a relatively low degree, that is, one whose higher order derivatives vanish. It is this basic assumption which allows one to interpolate sets of discrete data by the use of continuous functions. One is immediately in difficulty, however, with the problem that if each member of the set of discrete data was subject to randomly distributed errors, then one cannot know precisely which approximating function to

use, with some a priori knowledge. The interpolating process then becomes one of selecting a particular function from a family of functions (i.e., different polynomial degrees) which can be used, in a sense, to describe the experiment. For purposes of this discussion, this process is arbitrarily preselected in order to compare different functional degrees.

The process of selecting a particular function from a family of functions becomes difficult in view of the circumstances about the conduct of an experiment. For example, the statement is often made than an experimental variable can be observed to be within some tolerance, or precision, which shall be called e. Now, if one graphically displays a set of one of these variables against a second variable, assuming all the other observed quantities to be constant, one may obtain a plot such as illustrated in Figure 21. From Figure 21, the person analyzing the data would conclude either that some of the variables are in error in relation to a majority of the observations or that the data are indeed correct. If this latter viewpoint is accepted, then functions whose higher order derivatives exist must be used to interpolate the data. The consequences are that if a function which oscillates considerably is used to represent the data, then the basic assumption stated above is false, and the system may be said to exhibit certain peculiarities. If this hypothesis is accepted, then one usually re-evaluates the experimental data by further experimental work.

If the unexplained peculiarities do persist, then an attempt may be made to revise existing theory to explain these observations. In some of these cases, it is concluded that a fundamental physical law is fallacious.

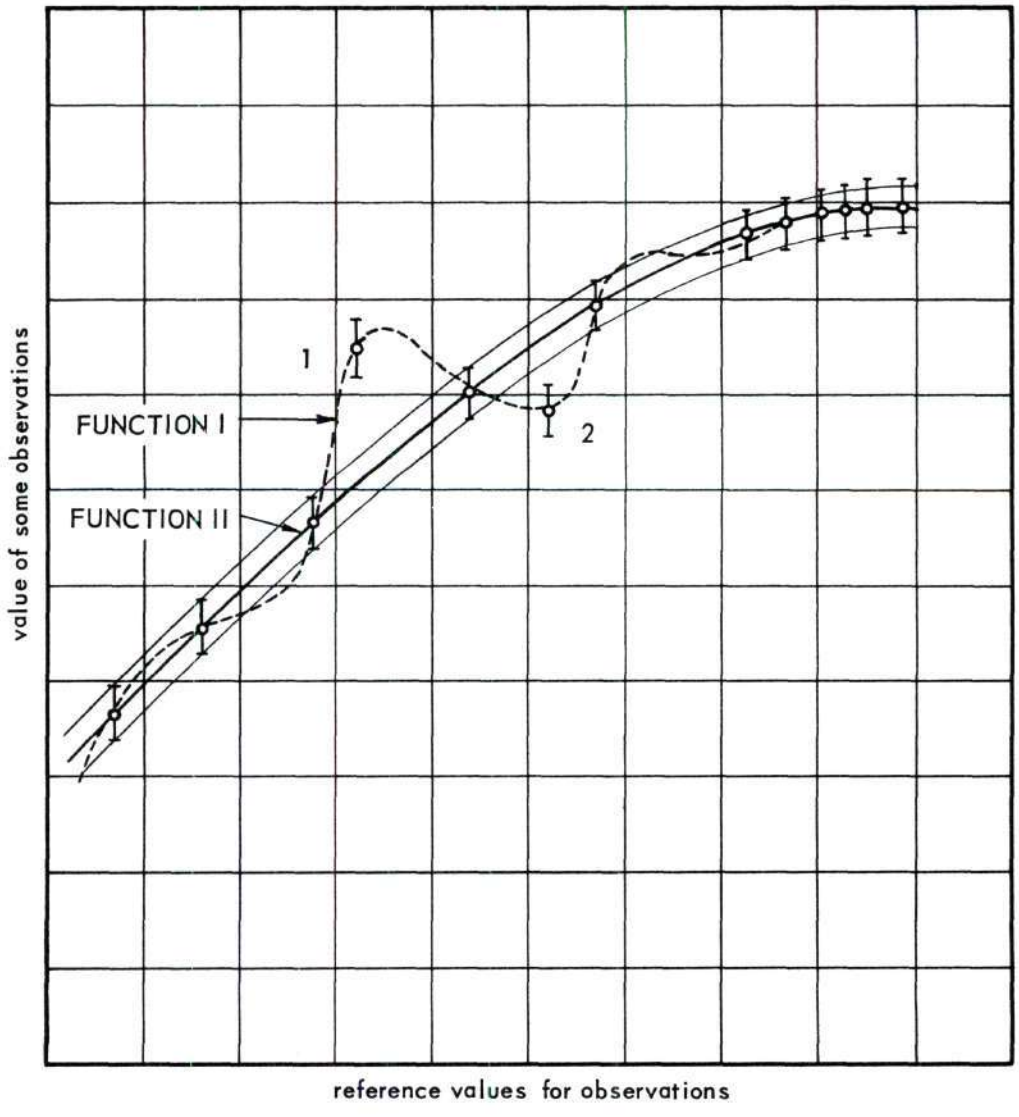


Figure 21. A plot of some observed quantities and two possible functional approximations depending on whether points 1 and 2 are considered to be in error.

It is usually more convenient, however, to hold the fundamental law inviolate and to assume that experimental error did in fact exist. A question might then arise, in that if one admits experimental error in one point of a set, then how many other points are subjected to an error greater than a stated precision? Even if one abandons the deterministic model of the real world and goes to a stochastic model in which, for a given set of values of the independent variables, it is assumed that the physical event to be observed will occur according to some probability distribution, one usually adopts the same point of view -- that is, if an observation is made which falls outside a probable range, it may be rejected as erroneous. The answer to the question of experimental error, however, must lie with the original experimentor who must evaluate some tolerance for each observation in a set of observations. Many investigators, indeed, do smooth the data prior to publication.

But, back to the question of what is the best approximating function to use. Forsythe (59) has proposed the use of a certain computable statistic for testing whether higher degree polynomials make a significant reduction in the norm criterion. However, little theoretical support can be found for using this test, and in practice cases have arisen in which several distinct reductions in the norm criterion were indicated.

If the fundamental law or physical model were understood, the selection of the form of the fitting function would be accomplished. It would then be an easy matter to select the criterion of best fit with respect to some particular functional form. If, however, one is given a set of data and then asked to fit an unspecified function to the data, it becomes painfully evident that there are usually not enough conditions to

insure the selection of a "best" fitting function.

In regard to the very particular problem of evaluating vapor-liquid equilibrium data, it is suggested that a method exists for ascertaining a best fitting criterion. The logic of the method will subsequently be developed.

An isothermal vapor-liquid equilibrium experiment yields 4 related quanta. They are the total pressure and temperature of the system, and the vapor and liquid compositions usually given in mole fractions of one of the binary components. Many authors use these data to compute such correlating quantities as the excess chemical potentials or the difference of the excess chemical potentials under isothermal or isobaric conditions. Since the computation of the excess chemical potentials involves the evaluation of the logarithm of the ratios of vapor to liquid compositions, these terms tend toward the indeterminant form 0/0, in the dilute regions.

Furthermore, it is then generally conceded that the experimental values in the dilute regions tend to be less accurate than the data for middle concentrations. Thus, it is felt that the use of the computations for the excess chemical potentials, as just described, for the evaluation of vapor-liquid equilibrium data becomes completely untenable.

It therefore becomes the prime contention of this author that the basic experimental data must be fitted by a function before any computations are performed. This must, of necessity, be the case because the experimental values are known precisely at the limits of the dilute regions -- the total pressure tends toward the vapor pressure of the pure components as the mole fractions of the constituents tends toward zero

or one. It is therefore proposed to find two fitting functions; one for the total pressure and the other for the vapor composition, with both in terms of the liquid compositions. The fitting function is an orthogonal polynomial where the best fit, for each degree, is in a least squares sense. The method proposed by Forsythe, which was previously discussed, is used. The criterion for the selection of the best degree of polynomial is discussed below.

From the polynomial approximations to the basic experimental data, values (or pseudo-data) of the total pressure and vapor compositions can be computed at equally spaced values of the liquid compositions. In addition, the derivatives of the total pressure and vapor compositions are also computed. Thus, with this interpolated data, Simpson's rule can be used to compute the integral of the difference of the excess chemical potentials. But better still, the value (or the deviation from zero) of the Gibbs-Duhem equation (more specifically equation (71)) can be computed at these discrete points. It is felt that the Gibbs-Duhem equation is the best criterion to use since, as was previously shown, one can obtain the integral of the difference of the chemical potentials to be zero and not have the Gibbs-Duhem criterion even close to being satisfied. The question of the best degree of polynomial, however, still remains unanswered.

It is therefore proposed to examine all the different possible combinations of degrees of fitting polynomials in light of the Gibbs-Duhem equation. That is, for each combination of degree of polynomial fit of total pressure and vapor compositions in terms of liquid composition, the deviation from zero in the Gibbs-Duhem equation will be computed. The criterion of using the sums of squares of deviations to the Gibbs-Duhem equation

is arbitrarily chosen because of the simplicity of its use. Other possible choices include criterion of having the absolute value of the integrand of the integral of the deviations from zero be a minimum, or using some least upper bound of the absolute value of the deviations of the Gibbs-Duhem equation. The sums of squares of these deviations will be computed for each possible pair of fitting polynomials. It is concluded that the best degree of polynomial fits to the original data occur when the sums of the squares of the deviations are a minimum. This, in effect, says that when given a set of experimental data, the criterion of best fit shall be when the data are representable in the best possible light with respect to the Gibbs-Duhem equation.

To summarize the preceding discussion, the proposed procedure involves the following steps.

1. Collect the isothermal data for a binary system, which consists of the total pressures, vapor compositions, liquid compositions, molal volumes, and vapor pressures of the pure components and the second virial coefficients.

2. Using the methods just described, obtain the best-fitting polynomials of all admissable degrees for the two cases: first the total pressure as a function of the liquid compositions, and second, the vapor composition as a function of the liquid compositions.

3. For each combination of these polynomials, evaluate the function in equation (71) at a large number of points, square and sum the results. Since this function theoretically vanishes identically, the resultant sum of squares is taken as a measure of the inconsistency of the vapor-liquid equilibrium data.

4. The two polynomials which give the smallest value for the sum of squares of the function of equation (71) are said to represent the data in the best possible manner with respect to thermodynamic consistency. This criterion is impartial.

5. If the smallest value of the sum of squares of the function (i.e., deviations from zero) is a small number, then the data are intuitively thermodynamically consistent. However, if the smallest value is still quite large, it cannot be guaranteed that the data are thermodynamically inconsistent.

The complete thermodynamic consistency test is demonstrated for the system, ethanol--benzene in Appendix C.

# CHAPTER VI

## DISCUSSION OF THE RESULTS OF THE CONSISTENCY TESTS

The entire procedure, which was discussed in the previous chapter was programmed for the Burroughs 220 computer. To make a complete test of the isothermal vapor-liquid equilibrium data for a given system takes approximately 1.5 $n^2$ minutes of computer running time, where n is the number of data points for a given system. Thus for a fifteen data point system computer time was just over five and one-half hours. For this reason, many systems were not tested in this thesis. The binary system, ethanol--benzene was tested in detail and the results are given in Appendix C. From the results for this system, it is concluded that the vapor-liquid equilibrium data of Brown and Smith (38) are thermodynamically consistent. For the fourteen data points given in reference (38), it appeared that a polynomial of degree eleven in vapor composition and of degree ten in total pressure gave the best fit of the experimental data. The data of Udovenko and Fatkoulina (62) could not be satisfactorily described by any of the polynomial combinations.

The values of the integrals of the differences of the excess chemical potentials were also computed for every polynomial combination. It was observed that, in the case of ethanol--benzene at 45° C., the value of the integral corresponding to the best fitting polynomials described above was not the absolute minimum. This result tends to substantiate some of the remarks made in the previous chapter concerning the use of the integral as a test of thermodynamic consistency. The value of the integral was -0.274

calories per gram-mole while the sum of squares of the deviations (as computed by equation (71)) was 83.4 calories per gram-mole at the best fit. The absolute minimum of the integral was -0.019 where the polynomial degree of the vapor composition was eight and of the total pressure was three. The value of the sums of squares of deviations from zero was 47,858.0 calories per gram-mole for this combination of polynomials -- clearly not the best in terms of thermodynamic consistency.

Some of the other systems that were investigated are now briefly summarized. The data of Ibl, et al. (63) for the system, pyridine--water at 30 and 50° C. could not be adequately fitted by any of the polynomials for 15 data points. A plot of this data revealed considerable scatter in the total pressure measurements which showed up as poor values of the derivatives in the fit of the total pressure data.

The vapor-liquid equilibrium data of Dornte (64) for the system, ethanol--water at 25° C. and of Beare, et al. (65) for the system, acetone--water at 25° C. could not be satisfactorily fitted by any polynomial combination. The data of Scatchard and Raymond (57) for ethanol--chloroform, which was used in the development of this procedure, was found to be thermodynamically consistent. These results are summarized in Table 26.

Table 26. A Summary of the Results of the Thermodynamic Consistency Tests.

| Binary System and Temperature | Number of Data Points | Degree of Best Fitting Polynomial For | | Sums of Squares of Deviations (Calories per gram-mole) |
|---|---|---|---|---|
| | | Total Pressure | Vapor Composition | |
| ethanol-benzene 45° C | 14 | 10 | 11 | 83.5 |
| ethanol-benzene 40° C | 13 | 10 | 11 | 3404 |
| ethanol-benzene 50° C | 13 | 10 | 11 | 670 |
| ethanol-benzene 60° C | 13 | 11 | 11 | 2344 |
| pyridine-water 30° C | 13 | 3 | 4 | 1646 |
| pyridine-water 40° C | 15 | 2 | 3 | 1246 |
| ethanol-water 25° C | 13 | 10 | 9 | 1468 |
| acetone-water 25° C | 15 | 8 | 9 | 1182 |
| ethanol-chloroform 45°C | 29 | 12 | 11 | 36.3 |
| ethanol-chloroform 45°C | 27 | 8 | 8 | 55.1 |
| ethanol-chloroform 55°C | 26 | 12 | 10 | 31.7 |

# CHAPTER VII

## CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

The following conclusions have been made from this study on eight ternary systems and twenty-one binary systems:

1. For ternary systems containing two partially miscible binary pairs and an ideal binary pair, the liquid phase equilibrium was satisfactorily predicted using the Margules model, the predictions being only slightly better than the van Laar model. The predicted distribution was very nearly the same as the experimentally determined distribution and the predicted binodal curve followed the experimental binodal curve very closely. This conclusion was based on the results of the following systems:

Furfural--n-heptane--cyclohexane

Aniline--n-heptane--cyclohexane

nitroethane--n-octane--isooctane

2. For ternary systems containing three immiscible binary pairs, it was possible for the Margules and van Laar equations to predict three separate binodal curves. This observation was based upon studies of the one system, decyl alcohol--nitromethane--ethylene glycol. The results of this system were quantitatively poor but nevertheless indicated the presence of three binodal curves.

3. For ternary systems containing one immiscible binary system and two non-ideal miscible systems, the phase composition predictions were good for the distribution curves where the composition of the third

miscible component was small. The predicted tie-lines in the concentrated regions of the ternary systems were not satisfactory, in that, in all cases the predicted system was less ideal than the actual system. These conclusions were based on the results for the following systems:

Benzene--water--pyridine

Benzene--water--ethanol

Chloroform--water--acetone

Nitromethane--n-heptane--benzene

4. The use of orthogonal polynomials provided a means of fitting the experimental data to any desired degree up to the number of data points less two. The total pressures and vapor compositions were fitted just as one would fair a curve through the data points on a graph. This is contrasted to the fact that the use of ordinary polynomials does not give good fits to vapor-liquid equilibrium data.

5. On the basis of the results of five isothermal binary systems, the test of thermodynamic consistency presented in this thesis provides a very accurate test for the evaluation of isothermal binary vapor-liquid equilibrium data. Its use is recommended over the integral tests when very accurate results are desired.

6. On the basis of the results of evaluating the parameters to the standard binary equations, discussed in this thesis, for nine non-ideal miscible systems, it was observed that the Margules three constant equation gave the best fit of the activity coefficient data in the least squares sense.

During the course of this investigation more questions have been raised than have been answered. A new area of exploration has become a

reality which only yesterday was a dream. The advent of the computer has made it possible for extensive numerical computations to be performed -- to conduct numerical experimentation on the theories of physical processes. While it must be said that the results presented in this work tend to be disappointing in their failure to satisfactorily predict ternary liquid-liquid equilibrium, these results do point out some needs in fundamental areas of study. They point out, for example, that more good isothermal binary vapor-liquid equilibrium data are needed, especially in the region of the critical solution temperature of partially miscible systems. For no matter how well the techniques of numerical experimentation are developed, good experimental data is the primary requisite for testing any mathematical model.

The fact that vapor composition and total pressure data can be fitted very well by orthogonal polynomials opens up many new areas of vapor-liquid equilibrium data analysis. Studies on the use of the Gibbs-Duhem equation for isobaric systems should be very fruitful in the near future. The use of these methods once again shows the necessity of having extremely good vapor-liquid equilibrium data to work with for the orthogonal polynomials as used in this thesis are very sensitive to scatter in the data.

Another area for future investigation is the testing of other mathematical models for the Gibbs excess free energy having a more theoretical basis than the empirical Wohl model used in this work. The extension to the prediction of ternary vapor-liquid equilibria becomes very feasible for if one can predict the activities at any ternary composition, then one can certainly predict the vapor composition in equilibrium with the liquid.

Also there is the intriguing problem of computing the parameters of the ternary model from a knowledge of the conjugate phase compositions only, in a manner similar to that used for partially miscible binary systems. Many fruitless hours have been spent by the author in this area of study, but new ideas are always waiting to be tried.

And finally the extension of all of these concepts to multi-component systems poses an inviting challenge for some future study.

# APPENDICES

# APPENDIX A

## THE CORRECTION FOR VAPOR PHASE IMPERFECTIONS

Of the many different equation-of-state forms described in the literature, the type most often used in vapor-liquid equilibrium computations is one involving the second virial coefficient when the pressures are low. The use of an equation-of-state, which is basically a power series expansion in the virial coefficients, truncated with the second virial coefficient gives a simple form with only one parameter to be determined. This is to be contrasted with the many parameters which are required in the use of other popular forms of equation-of-state, such as that of Beattie-Bridgman. While a many parameter equation is more exact, it is also more cumbersome to use, and the values of the parameters are not always available. Another point which will be discussed below, is that the combination laws for mixtures are only empirically developed. Finally, the use of the virial coefficients can be related to the development of equations-of-state from a study of intermolecular forces (66).

It is indeed unfortunate that there are many different virial equations-of-state in use. Thus before using any values from published virial coefficient data, one should ascertain the type of experiment that was conducted and which virial coefficient was obtained. This has not always been done in the published literature.

The virial equation-of-state which has some theoretical basis from statistical thermodynamics and is said to represent pressure-volume-temperature data fairly accurately is given by equation (85) (reference (67)).

$$P = \frac{RT}{V}\left(1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \ldots\right) \qquad (85)$$

where V is the molar volume of the pure substance, and B, C, and D, called the second, third and fourth virial coefficients, respectively, are functions of temperature only.

For gases at low pressures only the first two terms of equation (85) are retained.

$$P = \frac{RT}{V}\left(1 + \frac{B}{V}\right) \qquad (86)$$

It is also possible to represent the pressure-volume-temperature relationship by the following series expansion in pressure, (67)

$$V = \frac{RT}{P}\left(1 + B' P + C' P^2 + \ldots\right) \qquad (87)$$

where again the B' and C' are called the second and third virial coefficients. If higher terms than the first power of the pressure are neglected, one then gets equation (88)

$$V = \frac{RT}{P}\left(1 + B' P\right) \qquad (88)$$

where the units of B' are in reciprocal pressure units. The relationship between the pressure-explicit and volume-explicit second virial coefficients of equations (86) and (88) is given by

$$B = B' P V \qquad (89)$$

Another form of the virial equation has been used by Scatchard (57) which differs from both equations (86) and (87). Written in the volume explicit form as in equation (90), it gives the impression of a pressure series expansion.

$$V = \frac{RT}{P} + B'' \tag{90}$$

The units of B'' are of molar volume. The relationship of B'' to B of equation (86) is given by

$$B'' = \left(\frac{RT}{PV}\right) B \tag{91}$$

The term (PV/RT) is known as the compressibility factor, and at low temperatures and pressures it is approximately unity. It is perhaps for this reason that many authors do not even bother to make a distinction between the virial coefficients of equations (86) and (90).

Equation (90) is the virial equation-of-state used by Lambert and co-workers (69) where their method of determining the second virial coefficient was to first graphically display PV vs P data under isothermal conditions. Then from the slope and intercept, the second virial coefficient was determined by the following relation,

$$B'' = (RT/P_oV_o) \times (\text{Slope of PV vs P plot}) \tag{92}$$

When equation (86) is written for a binary mixture as

$$P = RT/V_m (1 + B_m/V_m) \tag{93}$$

the second virial coefficient of a binary mixture, as derived from statistical mechanics is given as a quadratic function of the mole fractions as in equation (94) (Reference (68)).

$$B_m = B_{11} y_1^2 + 2B_{12}y_1y_2 + B_{22}y_2^2 \tag{94}$$

$B_{12}$ can be considered to be that second virial coefficient manifested by a hypothetical substance which would be described by the same intermolecular

potential function as that which represents the interaction of the molecular species one and two.

Thus, with the assumption that the compressibility factor is unity, the volume-explicit virial equation, equation (90), becomes for a binary mixture

$$V = \frac{RT}{P} + B_{11}y_1^2 + 2B_{12}y_1y_2 + B_{22}y_2^2 \tag{28}$$

which is usually modified to the following form,

$$V = \frac{RT}{P} + B_{11}y_1 + B_{22}y_2 + R_{12}y_1y_2 \tag{29}$$

where

$$R_{12} = 2B_{12} - B_{11} - B_{22} \tag{30}$$

Substituting of equation (29) into equation (26) and performing the integration, with the assumption that the volume of the liquid is independent of the pressure, yields for a binary mixture equations (31) and (32) in terms of the activity coefficients.

$$RT \ln \gamma_1 = RT \ln \left( \frac{Py_1}{p_1^{\circ} x_1} \right) + (B_{11} - v_1^{\circ})(P - p_1^{\circ}) + R_{12}Py_2^2 \tag{31}$$

$$RT \ln \gamma_2 = RT \ln \left( \frac{Py_2}{p_2^{\circ} x_2} \right) + (B_{22} - v_2^{\circ})(P - p_2^{\circ}) + R_{12}Py_1^2 \tag{32}$$

Equations (31) and (32) have been used to such a great extent in vapor-liquid equilibrium calculations that, in effect, they are now standard. One should keep in mind all the assumptions used in their development

and that these equations are not the most precise and, in some instances, perhaps not even the best to use. The latter case is true when the contribution by the vapor phase imperfection terms of equations (31) and (32) is of the same order of magnitude as the logarithm term. This occurs when vapor-liquid equilibrium mixtures are very nearly ideal solutions. (The excess Gibbs free energy is small). It is also usually true that in these cases, the virial coefficients of mixing are not always available. For solutions which deviate greatly from ideal solutions, the contribution of the vapor phase imperfection terms become small when compared to the logarithm term.

The discussion up to this point has been to demonstrate the need of a volume explicit virial equation of state in the integration of the developed excess chemical potential equations. Subsequent discussions will deal with the methods of computing the second virial coefficients of pure substances and of mixtures.

Lambert, et al. (69) have shown that the Berthelot equation,[1]

$$B(T) = B - A/T^2 = (9R\,T_c/128P_c)\,(1-6\,(T_c/T)^2) \qquad (95)$$

agrees well with experimental measurements for many non-polar substances. The second virial coefficients of pure substances and binary mixtures of non-polar vapors can be successfully predicted by the application of the theorem of corresponding states (70). From a plot, representing the available measurements, of reduced second virial coefficients $(B/V_c)$ as a

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[1] In order to avoid confusion with the Berthelot equation parameter B, the second virial coefficient will henceforth be referred to as B(T) for the pure component and $B(T)_{12}$ for a binary mixture.

function of reduced temperatures, one finds this curve to be indistinguishable from a curve computed from the reduced Berthelot equation over a reduced temperature range of 0.65 to 1.00 (71). Therefore, we will relate our discussions about non-polar substances only to the Berthelot equation.

The experimental virial coefficients, when available as functions of temperature, are fitted by the method of least squares to an equation of the form,

$$B(T) = B - A/T^2 \qquad (96)$$

Equation (96) has been shown to agree well with experimental measurements for many non-polar substances at low pressures (69).

Our discussions of the treatment of pure substances was based on the fact that experimental virial coefficient data were available for most of the systems considered in this research. Even when virial coefficient data are not available, the computation is straight forward once it is decided to use the Berthelot equation. For mixtures, however, one is immediately in difficulty in that certain rules must be prescribed which are not in all cases verifiable. The following is a discussion of some of the rules for the computation of the second virial coefficients of a mixture based on a Berthelot equational form.

From a wide study of the properties of gaseous mixtures, two empirical rules have been suggested for the calculation of the Berthelot parameters, (A,B), of a mixture (72). The use of these rules presupposes that the second virial coefficient of the mixture, $B(T)_{12}$, representing the molecular interactions of molecular species 1 and 2, is computed by a

Berthelot type equation (equation (97)). Rule one is the Lorentz combination, equation (98), which approximately assumes that the distances of the minimums of the interaction functions are additive. Rule two, equation (99), follows from a simple interpretation of the dispersion forces. The name Lorentz-Berthelot mixture has been suggested for a mixture of Lennard-Jones molecules in which the parameters of the mixture are computed by these rules (72)

$$B(T)_{12} = B_{12} - A_{12}/T^2 \tag{97}$$

$$B_{12} = (B_{11}^{1/3} + B_{22}^{1/3})^3 / 8 \tag{98}$$

$$A_{12} = \sqrt{A_{11} A_{22}} \tag{99}$$

Another method suggested for the computation of the second virial coefficient of a binary mixture of non-polar substances is due to Scatchard and Ticknor (73). Their method is summarized briefly in the following section.

The $A_{12}$ and $B_{12}$ of equation (97) are treated similarly for a mixture as one would treat the a and b of van der Waals equation or the $A_o$ and $B_o$ of the Beattie-Bridgeman equation.

$$B_{12} = (B_{11}^{1/3} + B_{22}^{1/3})^3 / 8 \tag{98}$$

$$A_{12}/B_{12}^2 = \sqrt{\frac{A_{11}}{B_{11}^2} \cdot \frac{A_{22}}{B_{22}^2}} \tag{100}$$

Equation (98) is the Lorentz combination.

Equation (100) corresponds to a calculation of the energy density of a mixture from

$$(E/V)_{12} = \sqrt{(E/V)_{11}(E/V)_{22}} \tag{101}$$

where E is the energy difference between a perfect gas and the liquid state, and V is the volume of the liquid. This assumes that the separation of the molecules is proportional to the distance at which the interaction potential is a minimum and the energy of evaporation is approximately one-half of the minimum value of the interaction potential times the number of nearest neighbors in the liquid. Measurements of methane-butane mixtures have shown that values do fall between quadratic combinations of A/B, as given in equation (102), and $A_{12}/B_{12}^2$ as given in equation (100).

$$\frac{A_{12}}{B_{12}} = \sqrt{\frac{A_{11}}{B_{11}} \frac{A_{22}}{B_{22}}} \tag{102}$$

Of the two methods suggested for the computation of the second virial coefficient of the mixture, investigations were made by R. Techo to ascertain which might be the better one to use. These methods will be hereafter referred to as the Lorentz-Berthelot mixture rule as given by equations (98) and (99) and the Scatchard mixture rule as given by equations (98) and (100). Using the experimental data of Waelbroeck (74) for the second virial coefficients of mixtures of benzene-cyclohexane, the results have indicated that the Lorentz-Berthelot mixture rule was more suited to the prediction of the virial coefficients than the Scatchard rules. The Scatchard mixture rules gave values of $B(T)_{12}$ which were

approximately 50 per cent larger than the observed values. The A/B combination, equation (102) gave values of $B(T)_{12}$ that were 25 per cent greater than the observed values. The Lorentz-Berthelot mixture rules gave values of $B(T)_{12}$ which approximated the experimental data. The results of this investigation are summarized in Table 27.

The equations for the pure vapors were derived from a least squares fit of available experimental data, which is discussed below, and are summarized as follows:

$$B(T) = 48.8 - 12.8 \times 10^7 T^{-2} \quad \text{for benzene}$$

$$B(T) = 384 - 18.3 \times 10^7 T^{-2} \quad \text{for cyclohexane}$$

$$B(T)_{12} = 163 - 21.7 \times 10^7 T^{-2} \quad \text{Scatchard Rules}$$

$$B(T)_{12} = 163 - 18.3 \times 10^7 T^{-2} \quad \text{A/B combination}$$

$$B(T)_{12} = 163 - 15.3 \times 10^7 T^{-2} \quad \text{Lorentz-Berthelot mixture}$$

Table 27. A Summary of the Computations for the Second Virial Coefficients for the System Benzene--Cyclohexane.

(units are $cm^3/mole$)

| T°C | -B(T) Eqns. (98),(102) Scatchard Rules | -B(T) Eqns. (98),(102) A/B Comb. | -B(T) Eqns. (98)(99) Lorentz-Berthelot | $-B(T)_{12}$ Experiment |
|---|---|---|---|---|
| 30 | 2196 | | | |
| 40 | 2048 | | | |
| 50 | 1913 | | | |
| 55 | 1850 | 1532 | 1258 | 1227 |
| 60 | 1790 | | | 1203 |
| 65 | 1733 | 1433 | 1175 | 1158 |
| 70 | 1648 | | | 1109 |
| 75 | 1626 | 1343 | 1099 | 1075 |
| 80 | 1575 | | | |
| 90 | 1481 | | | |
| 100 | 1394 | | | |

The experimental data for this system indicate that the difference between $B(T)_{12}$ and $(B_{11} + B_{22})/2$ is negligible in that it is within the experimental error of each of the observed quantities. Thus for some non-polar mixtures, the assumption of $R_{12} = 0$ in equations (31) and (32) is a valid one. This can be considered as a simplification of the Lorentz-Berthelot mixture rules in certain cases. For mixtures where the critical constants of the two components do not differ too greatly, $R_{12} = 0$, has been observed to hold in the reduced temperature range of 0.5 to 0.8 (71).

Having discussed a method of computation of the virial coefficient of a mixture of non-polar vapors, one usually extends the discussion to mixtures of polar vapors. Instead the preceding discussion will be amplified and extended to polar mixtures in the following manner:

The various mixtures will be considered by the following classifications in the order presented for treatment in this investigation,

a. mixtures of non-polar vapors

b. mixtures of a non-polar and weakly polar vapors.

c. mixtures of non-polar and polar vapors

d. mixtures of polar vapors.

It is in part d. that the method of computation of the second virial coefficient of polar mixtures will be developed. The reason for this will become obvious in the development given below.

Non-polar--non-polar.--For mixtures composed only of non-polar molecules, the Lorentz-Berthelot mixture rule will be used for computing the second virial coefficient of the mixture. In addition to the above discussion of benzene-cyclohexane mixtures, there is ample evidence in the literature that the Lorentz-Berthelot mixture rule does approximate non-polar vapor mixtures reasonably well (72).

Non-polar--weakly polar.--For mixtures of a non-polar and weakly polar vapor, the Lorentz-Berthelot mixture rules will be assumed to hold. Perhaps the best argument in favor of its use is that it works (72). It has been observed that a number of weakly polar vapors, which possess a maximum energy of dipole interaction less than kT, show no measurable deviation from the principle of corresponding states even down to comparatively low reduced temperatures (71).

This can be explained by the fact that one of the conditions for a substance to conform to the principle of corresponding states requires that the molecules be spherical, either structurally or by virtue of rapid and free rotation. Thus when the temperature drops, the velocity of rotation decreases and the maximum energy of dipole interaction becomes larger than kT, thus increasing the possibility of a mutually favorable orientation forming a dimer of a fairly long life. This has not been observed in the case of weakly polar molecules (71).

Non-polar--polar.--For mixtures of non-polar and polar vapors, the second virial coefficient of the mixture should have the value predicted by the theorem of corresponding states, (i.e., the same as computed by the Lorentz-Berthelot mixture rules) since no specific mutual interaction between the unlike molecules should be expected. The degree of dimerization is assumed to be so small that interaction between the non-polar molecules and the dimer molecules of the polar vapor can be neglected (71).

Therefore, to compute the virial coefficient of a non-polar--polar mixture one would use the Lorentz-Berthelot combinatory rules assuming that each molecular species was described by the Berthelot equation corresponding to the theorem of corresponding states. Then the virial coefficient,

as a function of the mixture

$$B_m = y_1^2 B(T)_{11} + 2y_1y_2 B(T)_{12} + y_2^2 B(T)_{22} \qquad (94)$$

would be computed using the observed virial coefficients of each of the pure vapors. The virial coefficients of the polar molecules are expected to be considerably more negative than that predicted by the theorem of corresponding states.

Before considering the problem polar--polar interactions, some discussion of pure polar vapors will be pertinent. It should be noted that polar vapors deviate considerably from the principle of corresponding states at low reduced temperatures. Eucken (75) first proposed that polar vapors undergo partial association due to dipole interaction or hydrogen bonding, and that this is responsible for their deviation from the principle of corresponding states.

Lambert (71) has proposed that substances which deviate from the principle of corresponding states because of dimer formation due to dipole interaction or because of hydrogen bond formation, can be accounted for by a second virial coefficient of dimerization, $B_D = -RT/K_p$, where $K_p$ is the mass-action dissociation constant of the dimer. $K_p = \bar{p}^2$ (monomer)/ $\bar{p}$(dimer). This effect is then considered to be additive to the second virial coefficient as obtained from the principle of corresponding states.

Since experimental data are available for all the pure substances, which are polar, considered in this thesis, how can the work of Lambert be used in the computation of polar mixtures? On the surface, this method could only be used if a dimerization constant were available for the mutual

interaction of the unlike molecular species. Since such data are lacking for the systems under consideration here, this method cannot be used, but we shall use some of the ideas contained in the development of this method in subsequent discussions.

Another approach is the acknowledged successful empirical treatment of Stockmayer (76) whose computed second virial coefficients were successfully fitted to experimental data for pure polar vapors. This treatment does not, however, take into account the occurrence of long-life molecular association and has not been extended to binary mixtures (71). At present, the Lorentz-Berthelot mixture rules are assumed in most cases (68). Since experimental values for the pure vapors are available, this method is not considered in this research but it certainly warrants further study.

Instead, the combination rules proposed by Scatchard will be used for the following reasons: In mixtures of polar vapors, where each component shows a deviation from the theorem of corresponding states due to association or hydrogen bonding, it can be expected that the virial coefficient of the mixture will not follow the theorem of corresponding states. This deviation can be accounted for by dipole-dipole interaction between the dissimilar associated molecules or by hydrogen bonding between the individual dissimilar molecules, or combinations of the interactions. Deviations from the theorem of corresponding states are manifested by large negative values of the virial coefficients. It has been observed that the Scatchard rule predicts larger negative values for the second virial coefficient of a mixture than the Lorentz-Berthelot mixture rule. For the system acetone-nitromethane at 45° C, the following comparisons are made:

$B(T)_{12}$ = -3830 $cm^3/mol$ was obtained by Brown and Smith (77) from the isothermal vapor-liquid equilibrium data of the system.

$B(T)_{12}$ = -2800 $cm^3/mol$ was obtained by using the Scatchard rule where the data for each of the pure constituents were fitted to a Berthelot equation.

$B(T)_{12}$ = -2000 $cm^3/mol$ was calculated by Brown and Smith (77) using the Stockmayer potential with Lorentz-Berthelot mixture rules. The conclusion reached in this paper was the existence of a specific interaction between acetone and nitromethane molecules possibly involving hydrogen bonding between the oxygen of acetone and hydrogen of the nitromethane.

Thus, for the simplicity of computation, the Scatchard rule -- at least in this one case -- gives a value which is not unreasonable considering the uncertainties involved.

# APPENDIX B

## THE SECOND VIRIAL COEFFICIENTS FOR PURE SUBSTANCES

It is most desirable to have values for the second virial coefficients of mixing and of the pure constituents at the temperature the vapor-liquid equilibrium experiment is conducted. This is, however, rarely realizable, and the methods of estimation and extrapolation, which were discussed above, must be employed to extend any available data.

A survey of the literature revealed the following data for the pure substances involved in the binary and ternary systems under consideration in this research. It should be emphasized that an exhaustive literature survey was not made, the reasons being obvious.

Benzene.--Andon, et al. (80) determined the second virial coefficients for an equation of state similar to equation (78) using the experimental method of Baxendale, Enuestuen, and Stern (82).

Allen, et al. (79) published a Berthelot type equation (equation (96)) with the constants $B = 70$ cm$^3$/mole and $A = 12.3 \times 10^7$ cm$^3$-deg$^2$/mol where the virial coefficient was of the type used in equation (78).

Using all the data of Table 28, the following Berthelot type equation was fitted to the data by the method of least squares,

$$B(T) = 48.8 - 12.8 \times 10^7 \, T^{-2} \text{ cm}^3/\text{mol}$$

Equation (103) gives values of the virial coefficient which are about three per cent higher than those given by Allen, et al. (79), but these

Table 28. Second Virial Coefficient Data for Benzene

| $-B(T)$ $cm^3/mol$ | T° C. | Reference |
|---|---|---|
| 1366 | 30 | 79 |
| 1209 | 45 | 69 |
| 1265 | 45 | 78 |
| 1234 | 45 | 79 |
| 1194 | 50 | 79 |
| 1156 | 55 | 79 |
| 1100 | 55 | 69 |
| 1137 | 58 | 74 |
| 1117 | 60 | 74 |
| 1119 | 60 | 79 |
| 1080 | 61 | 69 |
| 1103 | 62 | 74 |
| 1084 | 65 | 79 |
| 1088 | 65 | 74 |
| 1046 | 67 | 80 |
| 1050 | 70 | 69 |
| 1051 | 70 | 79 |
| 1035 | 70 | 74 |
| 1019 | 75 | 79 |
| 1011 | 75 | 74 |
| 969 | 76 | 80 |
| 980 | 78 | 69 |
| 988 | 80 | 79 |
| 980 | 80 | 81 |
| 950 | 88 | 69 |
| 900 | 90 | 80 |
| 830 | 104 | 80 |
| 729 | 120 | 80 |

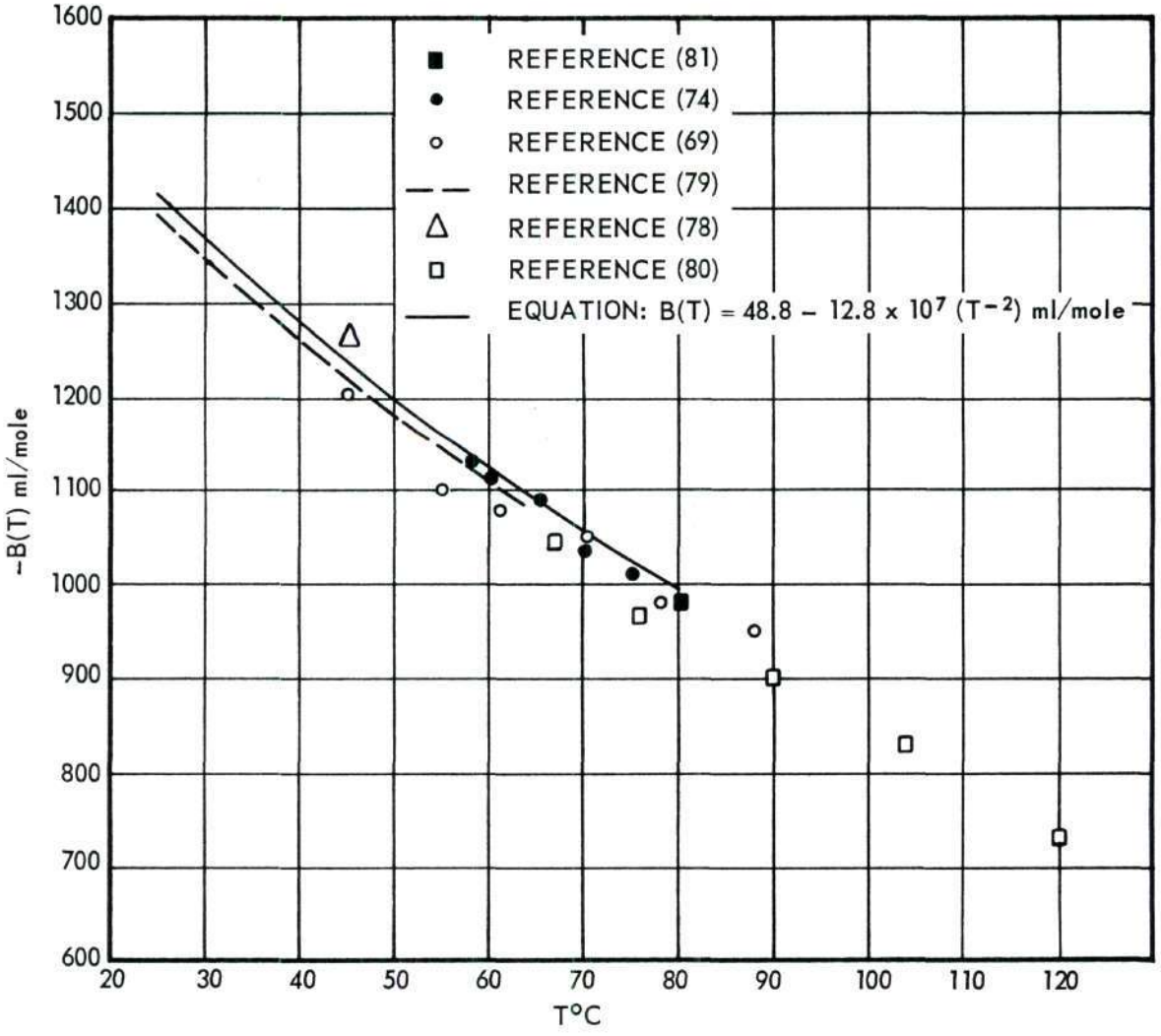


Figure 22. The second virial coefficient, B(T), as a function of temperature, °C., for benzene.

values are more consistent in view of the recent data of Waelbrock (74). Waelbrock (74) used a constant volume apparatus analogous to that of Eucken and Mayer (75) and the virial coefficients obtained were those for equation (85).

Table 29. Second Virial Coefficient Data for Cyclohexane

| $-B(T)$ $cm^3/mol$ | T° C. | Reference |
|---|---|---|
| 1518 | 42 | 74 |
| 1435 | 47 | 74 |
| 1382 | 50 | 74 |
| 1310 | 51 | 69 |
| 1355 | 55 | 74 |
| 1301 | 58 | 74 |
| 1268 | 60 | 74 |
| 1250 | 60 | 69 |
| 1260 | 62 | 69 |
| 1236 | 65 | 74 |
| 1110 | 65 | 69 |
| 1130 | 69 | 69 |
| 1180 | 70 | 74 |
| 1080 | 71 | 69 |
| 1080 | 71 | 69 |
| 1170 | 75 | 74 |
| 1100 | 78 | 69 |
| 920 | 89 | 69 |
| 900 | 109 | 69 |
| 800 | 131 | 69 |

Fit of data in the least squares sense, $B(T) = 384 - 18.3 \times 10^7 T^{-2}$ $cm^3/mol$ .

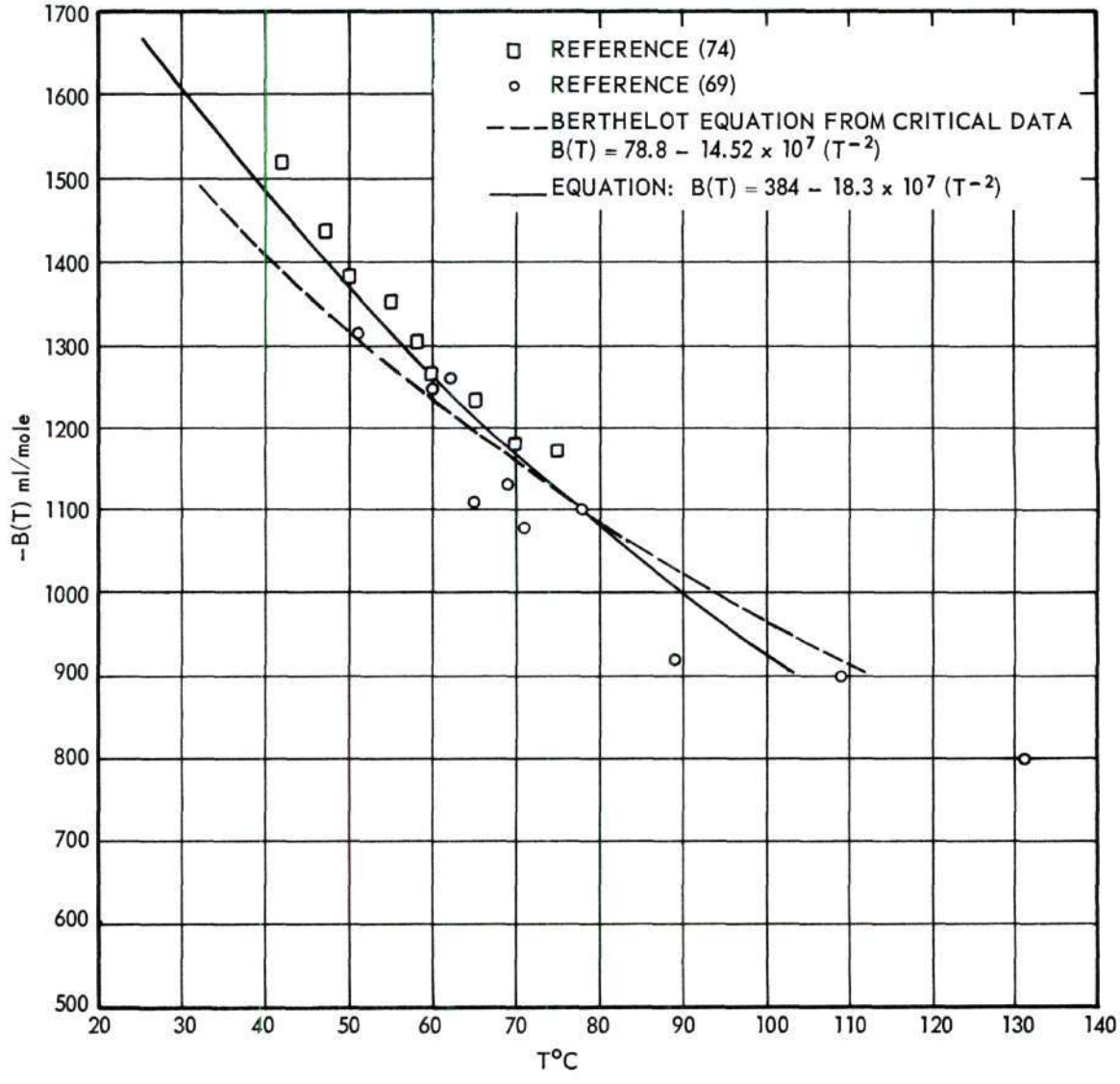


Figure 23. The second virial coefficient, B(T), as a function of temperature, °C., for cyclohexane.

Table 30. Second Virial Coefficient Data for Chloroform

| $-B(T)$ $cm^3/mol$ | T° C. | Reference |
|---|---|---|
| 950 | 45 | 69 |
| 1000 | 50 | 83 |
| 1000 | 52 | 69 |
| 950 | 58 | 69 |
| 900 | 62 | 69 |
| 830 | 70 | 69 |
| 840 | 70 | 83 |
| 790 | 78 | 69 |
| 730 | 90 | 83 |
| 690 | 101 | 69 |
| 630 | 110 | 69, 83 |

Fit of data in the least squares sense,

$B(T) = 57.4 - 9.89 \times 10^7 \, T^{-2}$ $cm^3/mol$ .

Ethanol.--Barker et al. (84) computed their values of the virial coefficient for ethanol from the experimental heat of vaporization data of Fiock, Ginnings and Holton (85) and vapor pressure data fitted to the Antoine equation. The following equation was used,

$$B(T) = \frac{\Delta H_v}{T} \left(\frac{dt}{dp}\right) + V_L - \frac{RT}{P} \qquad (104)$$

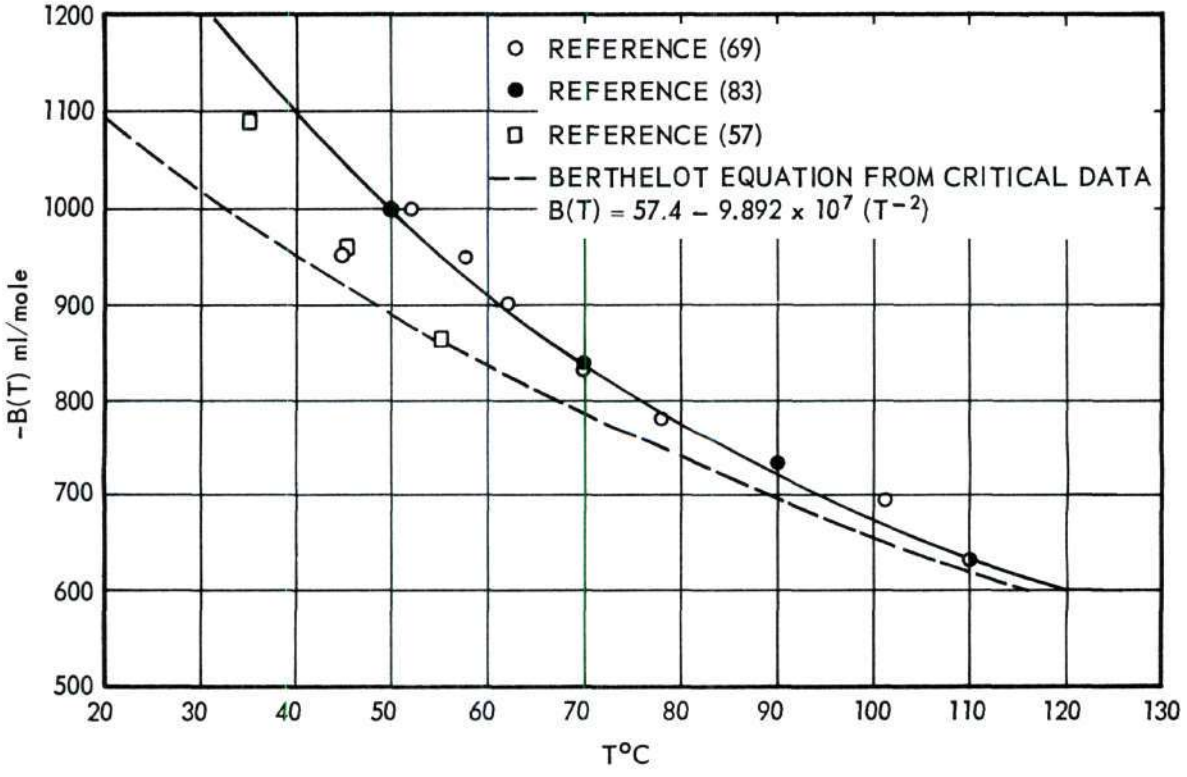


Figure 24. The second virial coefficient, B(T), as a function of temperature, °C., for chloroform.

Table 31. Second Virial Coefficient Data for Acetone

| $-B(T)$ $cm^3/mol$ | T° C. | Reference |
|---|---|---|
| 1640 | 44 | 69 |
| 1560 | 50 | 83 |
| 1520 | 55 | 69 |
| 1400 | 60 | 69 |
| 1380 | 68 | 69 |
| 1280 | 70 | 83 |
| 1250 | 77 | 69 |
| 1150 | 88 | 69 |
| 1040 | 90 | 83 |
| 950 | 94 | 69 |
| 850 | 110 | 83 |
| 840 | 110 | 69 |
| 700 | 130 | 83 |
| 600 | 133 | 69 |

Fit of data in the least squares sense,

$$B(T) = 953 - 26.4 \times 10^7 \, T^{-2} \ cm^3/mol \ .$$

Substitution of the Antoine equation for dp/dt gives,

$$B(T) = \frac{\Delta H_v \, (c + t)^2}{T \, (2.3026) \, bP} + V_L - \frac{RT}{P} \ . \qquad (105)$$

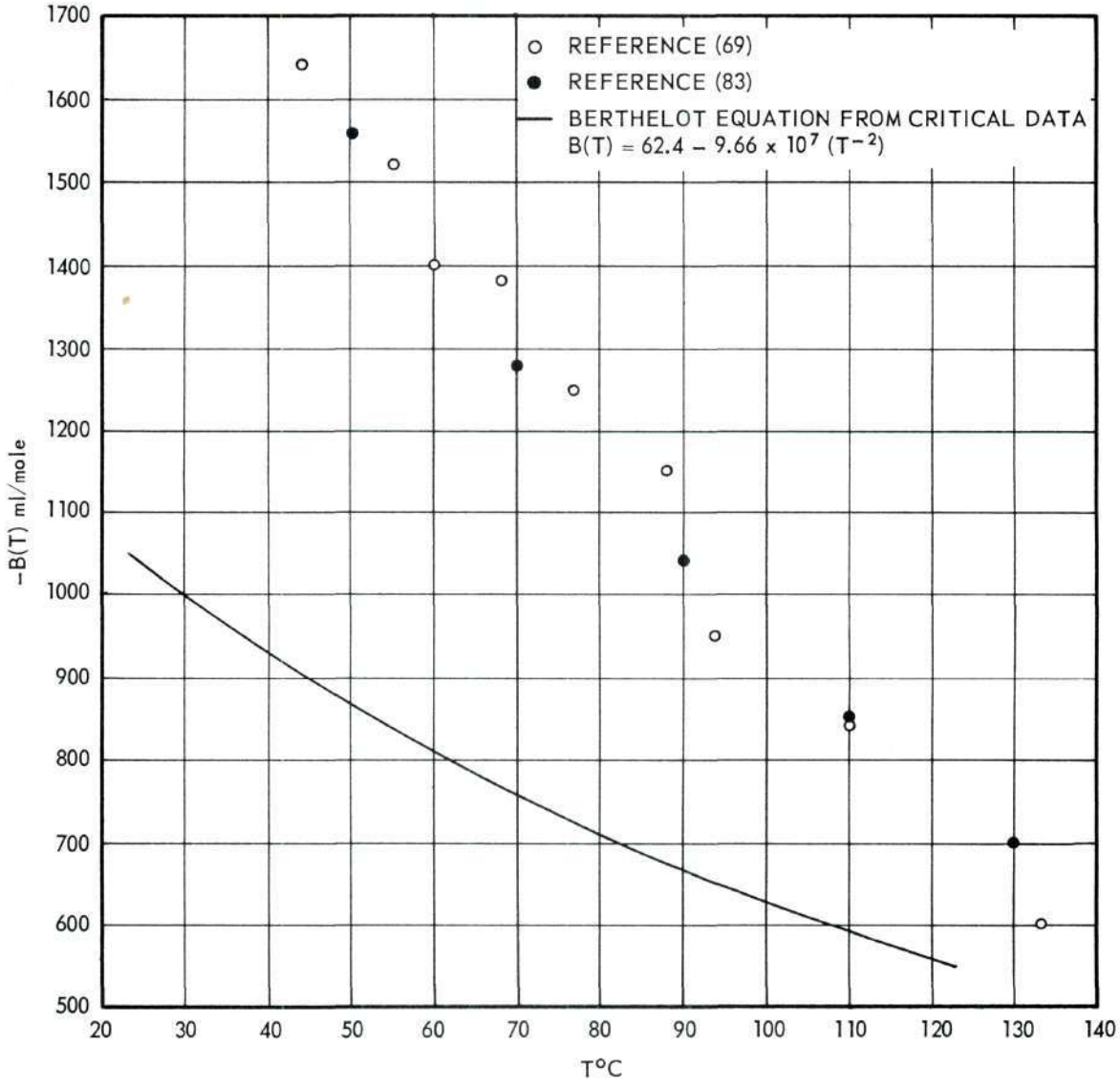


Figure 25. The second virial coefficient, B(T), as a function of temperature, °C., for acetone.

Table 32. Second Virial Coefficient Data for Ethanol

| $-B(T)$ $cm^3/mol$ | T° C. | Reference |
|---|---|---|
| 1965 | 45 | 84 |
| 2730 | 49 | 71 |
| 1990 | 59 | 71 |
| 1690 | 64 | 71 |
| 1615 | 65 | 84 |
| (1700) | 70 | 71 |
| 1360 | 71 | 71 |
| 1330 | 78 | 71 |
| 1150 | 88 | 71 |
| 930 | 98 | 71 |
| 680 | 109 | 71 |
| 420 | 126 | 71 |

It has been observed that computations such as given by equation (104) and (105) are not very exact since B is rarely more than five per cent of $V_L - \frac{RT}{P}$, which is the quantity directly calculated (72).

Scatchard and Raymond computed the second virial coefficients for ethanol from the equation, involving critical constants, proposed for water with the assumption that the theorem of corresponding states was valid. At temperatures of 40 to 50 degrees centrigrade their values were

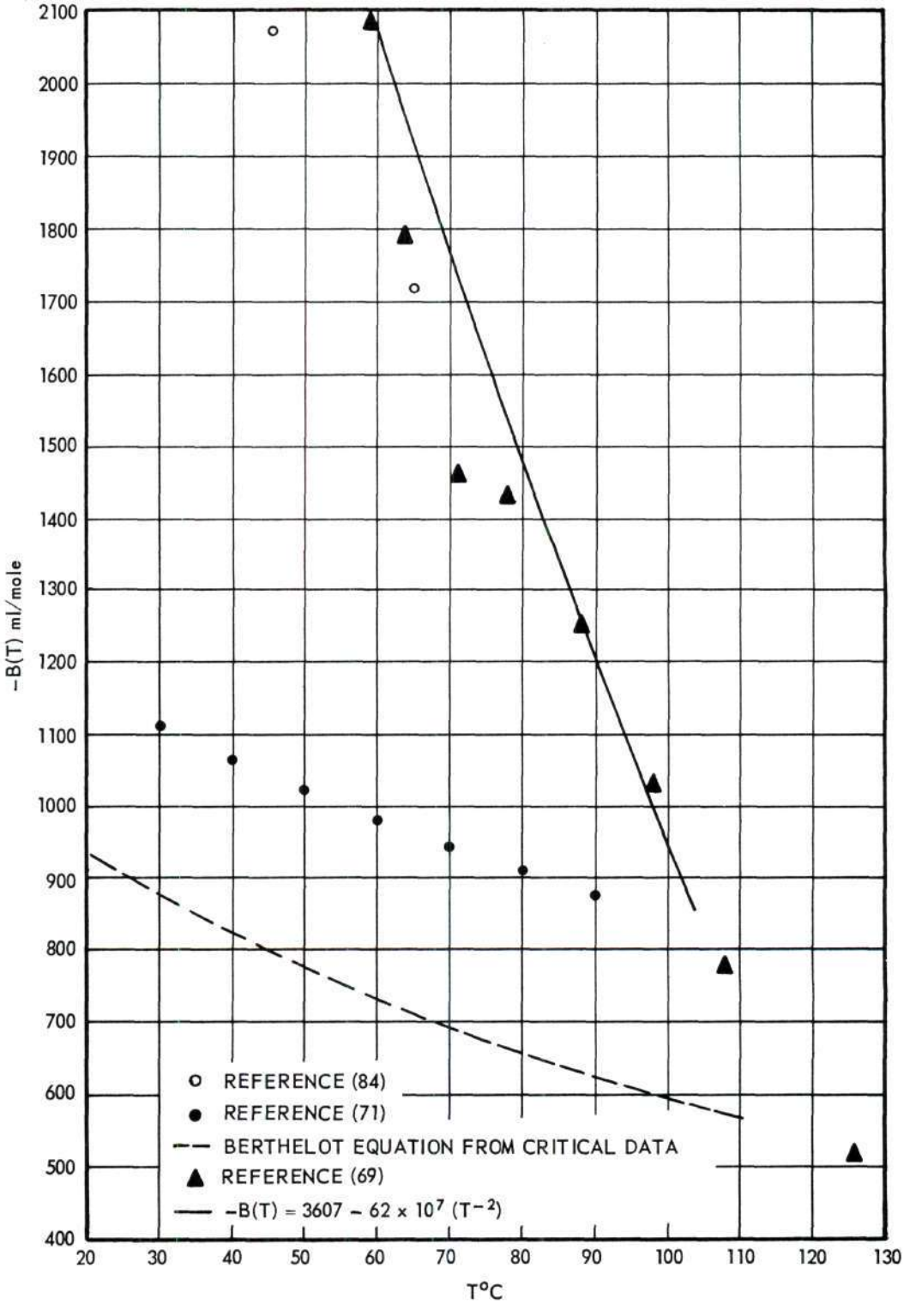


Figure 26. The second virial coefficient, B(T), as a function of temperature, °C., for ethanol.

approximately one-third those reported by Lambert (69).

The data of Table 37 has been fitted by the following Berthelot type equation using the method of least squares,

$$B(T) = 3607 - 62 \times 10^7 \, T^{-2} \ cm^3/mol \ .$$

Table 33. Second Virial Coefficient Data for Pyridine

| $-B(T)$ $cm^3/mol$ | T° C. | Reference |
|---|---|---|
| 1263 | 75.9 | 80 |
| 1132 | 89.8 | 80 |
| 1054 | 103.7 | 80 |
| 973 | 119.9 | 80 |

Fit of data in the least squares sense,

$$B(T) = 104 - 16.5 \times 10^7 \, T^{-2} \ cm^3/mol \ .$$

For nitromethane, the three-parameter equation proposed by McCullough et al. (86), was changed to the Berthelot form to be consistent with the computations of mixtures.

$$B(T) = -300 - 12.92 \ Exp \ (1700/T) \ cm^3/mol \qquad (106)$$

$$B(T) = 3645 - 68.2 \times 10^7 \, T^{-2} \ cm^3/mol \qquad (107)$$

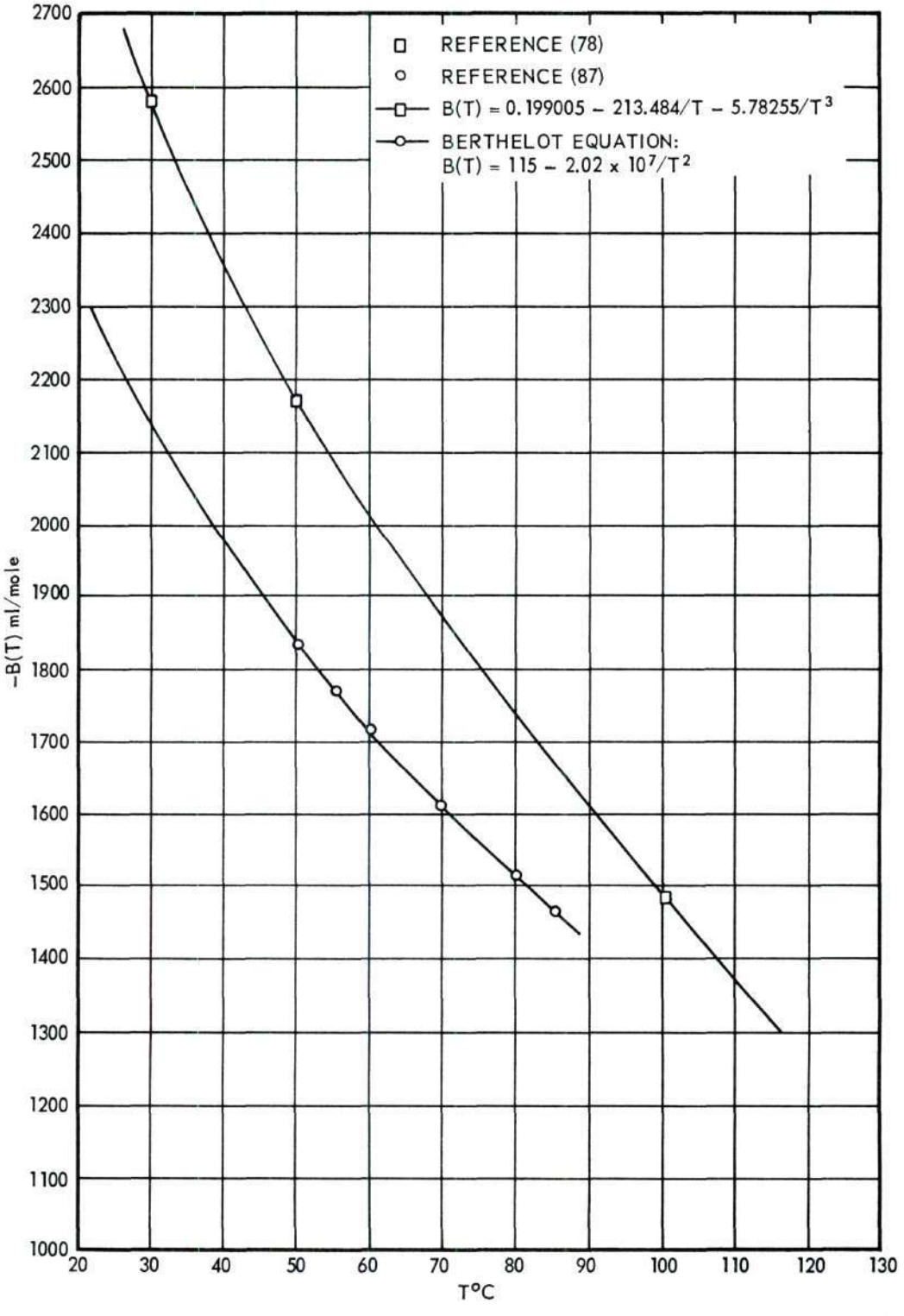


Figure 27. The second virial coefficient, B(T), as a function of temperature, °C., for n-heptane.

n-Heptane.--For n-heptane, there was an unexpected paucity of data. Reference (78) gave data of the second virial coefficients at temperatures which were too high to be of any use. Reference (23) gave an equation from unpublished sources (equation (108)). Brown and Ewald (87) computed the second virial coefficients from the Berthelot equation using critical constants.

$$B(T) = 0.199005 - 213.484/T - 5.78255 \times 10^7/T^3 \qquad (108)$$

Figure 26 shows the data computed by the methods of both references. It is noted that equation (108) gives virial coefficients considerably higher than those of the Berthelot equation. Since the source of equation (108) is unknown and Lambert et al. (69) has shown that the Berthelot equation yields fair results for non-polar substances, the Berthelot equational form with data derived from the critical constants will be used in this research (equation (109))

$$B(T) = 115 - 2.02 \times 10^7/T^2 \qquad (109)$$

# APPENDIX C

## THE BINARY SYSTEM, ETHANOL - BENZENE

Among the many sets of vapor-liquid equilibrium data available in the literature for the binary system, ethanol-benzene, the isothermal data of Brown and Smith (38) at 45° C. and that of Udovenko and Fatkoulina (62) at 40, 50, and 60° C. were selected for the correlation calculations to the standard binary activity coefficient equations. These were the only isothermal data which were found in the literature for this system. From an examination of a plot of the various parameters of the standard equations against reciprocal temperatures, considerable differences were observed between the data of reference (38) and that of (62) even when temperature differences were taken into account. Therefore a decision had to be made as to which was the better set of data. The term "better" is used in the sense of being more thermodynamically consistent.

The nature of the differences in the data was indicated from a plot of the isothermal vapor compositions against liquid compositions. It was noted that the 45 degree isotherm did not fall between the 40 and 50 degree isotherms as one would expect. Instead there appeared to be a shift of the data of reference (38) when contrasted to that of (62) resulting in considerable differences in the slopes of the curves.

The various constants used in the computations of the excess chemical potentials, from equations (31) and (32), other than total pressures and compositions, are summarized in Table 34. The virial coefficients of each of the components were computed from a Berthelot-type equation

(equation (96)) which was fitted to the available experimental data as shown in Appendix B. The virial coefficients of the mixture were computed from the assumed mixture law for non-polar-polar vapor mixtures as discussed in Appendix A.

All the sets of isothermal experimental data for the system, benzene-ethanol were tested for thermodynamic consistency by the method outlined in Chapter V. The results of these computations are summarized in the following paragraphs.

Using the 45 degree isothermal data of reference (38), the polynomials which gave the smallest sums of squares of deviations for the Gibbs-Duhem equation were of degree eleven explicit in the vapor composition and of degree ten explicit in the total pressure. Tables 35 and 36 indicate the fits obtained by these polynomials to the observed data. Table 37 summarizes the values of the sums of squares of residuals and the standard deviations for the different degrees of fitting polynomials. It should be noted that in this particular instance the selection of fitting polynomials using least squares theory would indicate polynomials of degree eleven in both cases on the basis of the smallest standard deviation. At best, however, the selection would be difficult to justify. The use of the additional condition imposed by the Gibbs-Duhem equation make the selection automatic.

For the selected polynomials, the sum of squares of deviations from zero for the Gibbs-Duhem equation was 83.5 calories per gram-mole. The integral of the excess chemical potential differences was -0.27 calories per gram-mole. A summary of the computations appears in Tables 38

through 41. The values of Table 40 are plotted in Figure 27. From an examination of Figure 27, it would appear that more data were required in the dilute alcohol concentrations. This data is considered to be thermodynamically consistent in view of the other systems studied in this thesis.

Table 34. Summary of the Constants Used In the Excess Chemical Potential Computations for Ethanol (1)--Benzene (2).

| T° C | $V_1$ | $V_2$ | $-B(T)_1$ | $-B(T)_2$ | $-B(T)_{12}$ | $P_1^\circ$ | $P_2^\circ$ |
|---|---|---|---|---|---|---|---|
| | liters/mol | | | liters/mol | | mm. Hg. | |
| 40 | 0.060 | 0.091 | 2.063 | 1.261 | .952 | 134.02 | 182.78 |
| 45 | 0.060 | 0.092 | 1.967 | 1.219 | .921 | 172.87 | 223.74 |
| 50 | 0.060 | 0.092 | 1.875 | 1.181 | .891 | 220.91 | 271.28 |
| 60 | 0.061 | 0.093 | 1.703 | 1.144 | .836 | 351.48 | 391.47 |

Testing the isothermal data of reference (62), it was found that there were no combinations of fitting polynomials which gave sums of squares of deviations for the Gibbs-Duhem equation to be less than 600 calories per gram-mole at any of the three temperatures (40, 50, and 60° C.). It was therefore concluded that these data could not be satisfactorily fitted by these orthogonal polynomials within the consistency criterion. The polynomials which gave the smallest sums of squares of deviations for each temperature are summarized in Table 42.

Table 35. Fit of Vapor Composition $y_1$ (ethanol) to the Liquid Composition $x_1$ by a polynomial of Degree Eleven for the System Ethanol (1)--Benzene (2).

| $x_1$ Liquid Composition | $y_1^*$ Vapor Composition (Observed) | $y_1$ Vapor Composition (Computed) | Difference $y_1 - y_1^*$ | Derivative $dy/dx$ |
|---|---|---|---|---|
| .0000 | .0000 | -.00000 | -.00000 | 8.18 |
| .0374 | .1965 | .19651 | .00001 | 3.08 |
| .0972 | .2895 | .2894 | -.00002 | .68 |
| .2183 | .3370 | .33704 | .00004 | .30 |
| .3141 | .3625 | .36240 | -.00009 | .23 |
| .4150 | .3842 | .38432 | .00012 | .20 |
| .5199 | .4065 | .40714 | .00064 | .23 |
| .5284 | .4101 | .40920 | -.00089 | .24 |
| .6155 | .4343 | .43460 | .00030 | .34 |
| .7087 | .4751 | 47492 | -.00017 | .52 |
| .8102 | .5456 | .54568 | .00008 | .93 |
| .9193 | .7078 | .70774 | -.00005 | 2.30 |
| .9591 | .8201 | .82014 | .00004 | 3.44 |
| 1.0000 | 1.0000 | .99999 | -.00000 | 5.58 |

Sums of squares of residuals = 0.00000.39

Standard deviation = 0.00068

Table 36. Total Pressure, P, to Liquid Composition, $x_1$, by a Polynomial of Degree Ten for the System Ethanol (1)--Benzene (2).

| $x_1$, Liquid | Total mm. Hg. (observed) | Total mm. Hg. (computed) | Difference | Derivatives dp/dx |
|---|---|---|---|---|
| .0000 | 223.51 | 223.515 | .005 | 1865.17 |
| .0374 | 271.01 | 270.992 | -.017 | 804.78 |
| .0972 | 296.53 | 296.554 | .024 | 191.51 |
| .2183 | 306.55 | 306.508 | -.041 | 44.43 |
| .3141 | 309.33 | 309.390 | .060 | 14.71 |
| .4150 | 309.59 | 309.542 | -.047 | -9.36 |
| .5199 | 307.46 | 307.383 | -.076 | -34.75 |
| .5284 | 306.99 | 307.075 | .085 | -37.81 |
| .6155 | 302.05 | 302.088 | .038 | -79.86 |
| .7087 | 291.81 | 291.746 | -.063 | -146.50 |
| .8102 | 271.08 | 271.130 | .050 | -274.86 |
| .9193 | 227.72 | 227.669 | -.050 | -547.52 |
| .9591 | 203.28 | 203.319 | .039 | -677.26 |
| 1.0000 | 172.87 | 172.861 | -.008 | -811.02 |

Sums of squares of residuals = 0.034

Standard deviation = 0.092

Table 37. Listing of the Sums of Squares of Residuals, $r_i$, and the Standard Deviations (S. D.) for Various Degrees of Fitting Polynomials for the Fourteen Isothermal Data Points of the System: Ethanol (1)--Benzene (2) at 45° C.

| Polynomial Degree | Vapor Composition | | Total Pressure | |
|---|---|---|---|---|
| | $r_i$ | S.D. | $r_i$ | S.D. |
| 2 | 0.10064 | 0.092 | 1747.0 | 12.1 |
| 3 | 0.0157 | 0.038 | 1741.0 | 12.6 |
| 4 | 0.0157 | 0.039 | 431.0 | 6.6 |
| 5 | 0.0027 | 0.017 | 208.0 | 4.8 |
| 6 | 0.0019 | 0.016 | 62.9 | 2.8 |
| 7 | 0.00039 | 0.0075 | 15.9 | 1.5 |
| 8 | 0.00015 | 0.0050 | 4.5 | 0.87 |
| 9 | 0.000020 | 0.0020 | 0.29 | 0.24 |
| 10 | 0.0000055 | 0.0012 | 0.034 | 0.092 |
| 11 | 0.0000014 | 0.00068 | 0.012 | 0.063 |
| 12 | 0.0000012 | 0.00078 | 0.011 | 0.075 |
| 13 | 0.0000012 | 0.00110 | 0.011 | 0.106 |

Table 38. Constants for the Computation of Interpolated Values, by the Orthorgonal Polynomials, for the Vapor Composition and Total Pressures for the System Ethanol-Benzene at 45° C.

| | Vapor Coefficients $c_i$ | Pressure Coefficients $c_i$ | Abscissa $\alpha_i$ | Coefficients $\beta_i$ |
|---|---|---|---|---|
| 1 | .45494285 | 271.412850 | .51022142 | .000000000 |
| 2 | .67931532 | -62.220953 | .49077333 | .109773580 |
| 3 | .46576979 | -399.705500 | .50448958 | .079584237 |
| 4 | 3.62764760 | -29.461727 | .48994755 | .052743626 |
| 5 | -.26534868 | -1758.340600 | .51658813 | .065661236 |
| 6 | 21.64347600 | 2832.025300 | .48621521 | .065764707 |
| 7 | -18.54010900 | -8319.782400 | .52357472 | .075490990 |
| 8 | 117.05698000 | 20405.142000 | .49020631 | .053665861 |
| 9 | -196.88474000 | -42473.388000 | .48083916 | .055897825 |
| 10 | 591.23090000 | 106456.850000 | .44341065 | .059260129 |
| 11 | -756.95626000 | | .58068226 | .070028007 |

$$\text{Where } y_k(x) = \sum_{i=0}^{k} c_i P_i(x)$$

$$\text{and } P_i(x) = (x - \alpha_i)P_{i-1}(x) - \beta_{i-1} P_{i-2}(x)$$

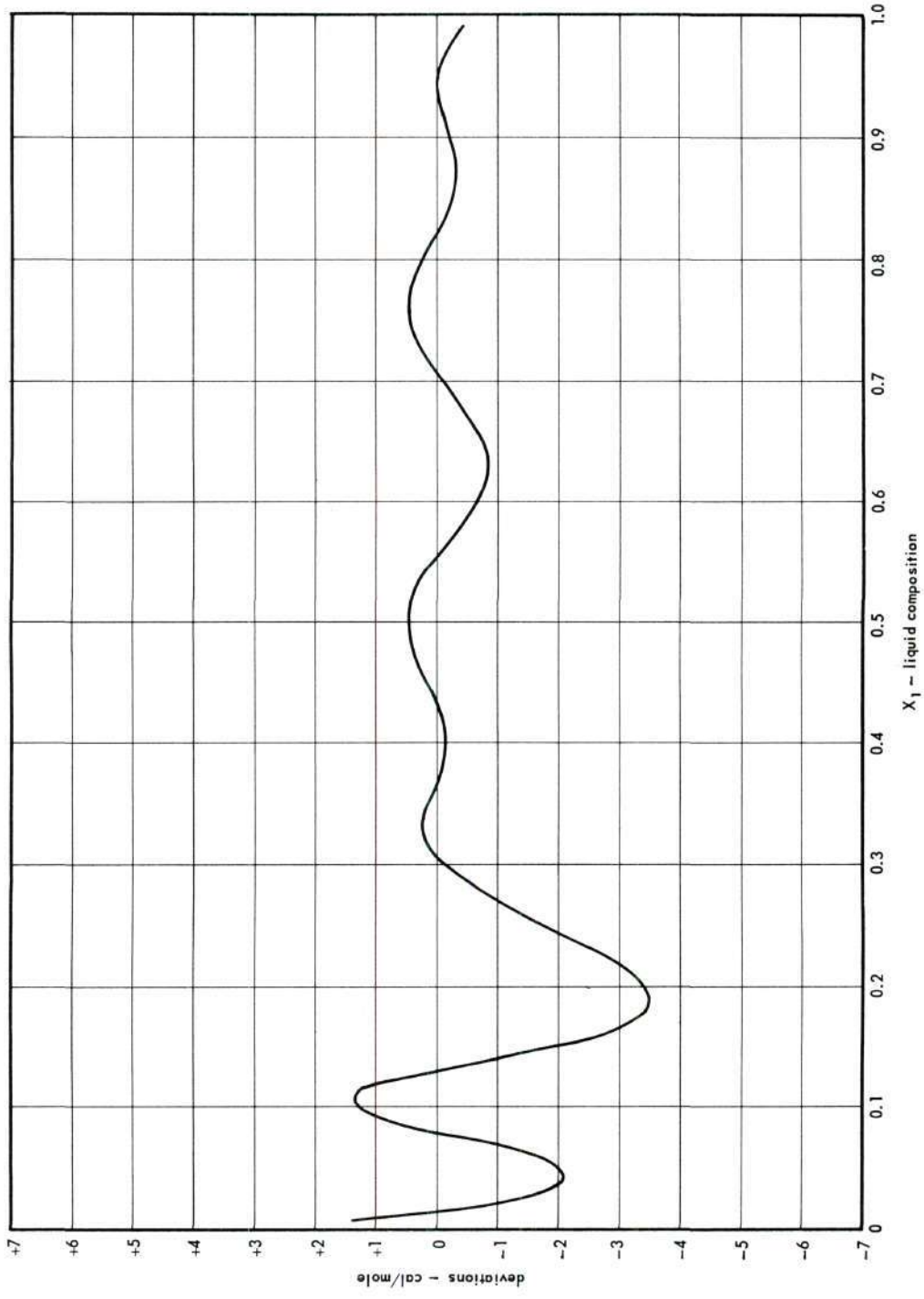


Figure 28. A plot of the deviation from zero of the Gibbs-Duhem equation (equation (71)) for the system: ethanol--benzene at 45°C. using tenth and eleventh degree polynomials to represent the total pressure and vapor compositions respectively.

Table 39. Interpolated Values of the Vapor Composition and Total Pressure and Their Derivatives for the System Ethanol (1) - Benzene (2) at 45° C. Using the Polynomials of Table 37.

| | $x_1$ | $y_1$ | $dy/dx_1$ | p (mm. Hg.) | $dp/dx_1$ |
|---|---|---|---|---|---|
| 1 | .010 | .0722 | 6.346 | 240.28 | 1500.89 |
| 2 | .020 | .1282 | 4.896 | 253.74 | 1201.10 |
| 3 | .030 | .1712 | 3.760 | 264.49 | 956.00 |
| 4 | .040 | .2042 | 2.878 | 273.02 | 757.06 |
| 5 | .050 | .2295 | 2.200 | 279.76 | 596.84 |
| 6 | .060 | .2488 | 1.685 | 285.06 | 468.87 |
| 7 | .070 | .2636 | 1.298 | 289.22 | 367.61 |
| 8 | .080 | .2751 | 1.011 | 292.49 | 288.25 |
| 9 | .090 | .2841 | .802 | 295.05 | 226.73 |
| 10 | .100 | .2913 | .652 | 297.07 | 179.58 |
| 20 | .200 | .3314 | .314 | 305.65 | 49.24 |
| 30 | .300 | .3590 | .240 | 309.15 | 19.23 |
| 40 | .400 | .3811 | .210 | 309.66 | -6.54 |
| 50 | .500 | .4025 | .226 | 308.00 | -28.33 |
| 60 | .600 | .4293 | .326 | 303.25 | -71.02 |
| 70 | .700 | .4704 | .507 | 292.98 | -139.00 |
| 80 | .800 | .5364 | .871 | 273.84 | -257.36 |
| 90 | .900 | .6670 | 1.927 | 237.66 | -488.55 |
| 91 | .910 | .6872 | 2.111 | 232.62 | -518.66 |
| 92 | .920 | .7093 | 2.319 | 227.28 | -549.72 |
| 93 | .930 | .7337 | 2.554 | 221.62 | -581.60 |
| 94 | .940 | .7605 | 2.821 | 215.65 | -614.11 |
| 95 | .950 | .7902 | 3.127 | 209.34 | -647.06 |
| 96 | .960 | .8232 | 3.479 | 202.70 | -680.25 |
| 97 | .970 | .8600 | 3.887 | 195.74 | -713.45 |
| 98 | .980 | .9012 | 4.363 | 188.44 | -746.44 |
| 99 | .990 | .9475 | 4.921 | 180.81 | -779.03 |

Table 40. Computed Values of the Gibbs-Duhem Equation for the System Ethanol (1)--Benzene (2) at 45° C.

| $x_1$ | $y_1$ | $x_1 \frac{\partial \mu_1}{\partial x_1} + x_2 \frac{\partial \mu_2}{\partial x_1}$ |
|---|---|---|
| .01 | .0723 | 1.08 |
| .02 | .1282 | -.37 |
| .04 | .2043 | -1.54 |
| .05 | .2295 | -1.50 |
| .06 | .2488 | -1.20 |
| .07 | .2636 | -.80 |
| .08 | .2751 | -.43 |
| .09 | .2841 | -.24 |
| .10 | .2914 | -.31 |
| .11 | .2973 | -.67 |
| .12 | .3024 | -1.25 |
| .13 | .3068 | -1.92 |
| 14 | .3109 | -2.53 |
| .15 | .3146 | -2.96 |
| .16 | .3182 | -3.18 |
| .17 | .3216 | -3.18 |
| .18 | .3250 | 2.99 |
| .19 | .3282 | -2.67 |
| .20 | .3314 | -2.27 |
| .21 | .3345 | -1.82 |
| .22 | .3376 | -1.38 |
| .23 | .3405 | -.97 |
| .24 | .3434 | -.61 |
| .25 | .3462 | -.33 |
| .26 | .3489 | -.12 |
| .27 | .3516 | -.00 |
| .28 | .3541 | .04 |
| .29 | .3566 | .03 |
| .30 | .3591 | -.03 |
| .31 | .3614 | -.14 |
| .32 | .3638 | -.27 |
| .33 | .3660 | -.40 |
| .34 | .3683 | -.51 |
| .35 | .3705 | -.60 |
| .36 | .3727 | -.65 |
| .37 | .3748 | -.67 |
| .38 | .3770 | -.65 |
| .39 | .3791 | -.59 |
| .40 | .3812 | -.50 |
| .41 | .3833 | -.39 |
| .42 | .3854 | -.27 |

Table 40. (Continued)

| $x_1$ | $y_1$ | $x_1 \frac{\partial \mu_1}{\partial x_1} + x_2 \frac{\partial \mu_2}{\partial x_1}$ |
|---|---|---|
| .43 | .3875 | -.15 |
| .44 | .3896 | -.03 |
| .45 | .3917 | .05 |
| .46 | .3938 | .12 |
| .47 | .3959 | .17 |
| .48 | .3981 | .18 |
| .49 | .4003 | .17 |
| .50 | .4025 | .13 |
| .51 | .4048 | .07 |
| .52 | .4072 | .00 |
| .53 | .4096 | -.20 |
| .54 | .4121 | -.14 |
| .55 | .4147 | 0.20 |
| .56 | .4174 | -.26 |
| .57 | .4202 | -.29 |
| .58 | .4231 | -.31 |
| .59 | .4262 | -.31 |
| .60 | .4294 | -.29 |
| .61 | .4327 | -.26 |
| .62 | .4362 | -.22 |
| .63 | .4398 | -.18 |
| .64 | .4437 | -.13 |
| .65 | .4476 | -.09 |
| .66 | .4518 | -.05 |
| .67 | .4562 | -.02 |
| .68 | .4607 | -.00 |
| .69 | .4655 | .00 |
| .70 | .4704 | .01 |
| .71 | .4756 | .00 |
| .72 | .4810 | -.01 |
| .73 | .4867 | -.03 |
| .74 | .4927 | -.05 |
| .75 | .4990 | -.07 |
| .76 | .5057 | -.08 |
| .77 | .5127 | -.09 |
| .78 | .5201 | -.09 |
| .79 | .5280 | -.09 |
| .80 | .5365 | -.07 |
| .81 | .5455 | -.05 |
| .82 | .5552 | 0.02 |

Table 40. (Continued)

| $x_1$ | $y_1$ | $x_1 \frac{\partial \mu_1}{\partial x_1} + x_2 \frac{\partial \mu_2}{\partial x_1}$ |
|---|---|---|
| .83 | .5656 | .00 |
| .84 | .5768 | .02 |
| .85 | .5889 | .04 |
| .86 | .6020 | .05 |
| .87 | .6162 | .05 |
| .88 | .6317 | .03 |
| .89 | .6486 | .00 |
| .90 | .6670 | -.03 |
| .91 | .6872 | -.07 |
| .92 | .7094 | -.12 |
| .93 | .7337 | -.16 |
| .94 | .7606 | -.20 |
| .95 | .7903 | -.22 |
| .96 | .8233 | -.23 |
| .97 | .8600 | -.22 |
| .98 | .9012 | -.19 |
| .99 | .9476 | -.16 |

Table 41. Computed Excess Chemical Potentials for the System, Ethanol (1)--Benzene (2) Using the Polynomials Giving the Minimum Sums of Squares of Deviations to the Gibbs-Duhem Equation.

| $x_1$ | $y_1$ | RT ln $\gamma_1$ | RT ln $\gamma_2$ | $\mu_1^E$ | $\mu_2^E$ | $\mu_1^E - \mu_2^E$ |
|---|---|---|---|---|---|---|
| .01 | .0723 | 60.23 | .16 | 1463.46 | 3.38 | 1460.08 |
| .02 | .1282 | 58.52 | .23 | 1420.55 | 4.51 | 1416.04 |
| .03 | .1713 | 56.57 | .25 | 1372.28 | 4.89 | 1367.38 |
| .04 | .2043 | 54.49 | .29 | 1320.95 | 5.62 | 1315.33 |
| .05 | .2295 | 52.35 | .36 | 1268.21 | 7.14 | 1261.07 |
| .06 | .2488 | 50.19 | .47 | 1215.31 | 9.56 | 1205.75 |
| .07 | .2636 | 48.05 | .60 | 1163.15 | 12.82 | 1150.33 |
| .08 | .2751 | 45.97 | .77 | 1112.41 | 16.76 | 1095.64 |
| .09 | .2841 | 43.96 | .95 | 1063.56 | 21.24 | 1042.32 |
| .10 | .2914 | 42.05 | 1.16 | 1016.94 | 26.10 | 990.83 |
| .20 | .3314 | 28.06 | 3.46 | 677.03 | 81.78 | 595.25 |
| .30 | .3591 | 19.86 | 6.14 | 477.88 | 146.83 | 331.06 |
| .40 | .3812 | 13.96 | 9.29 | 334.43 | 223.34 | 111.09 |
| .50 | .4025 | 9.42 | 12.99 | 224.13 | 313.32 | -89.19 |
| .60 | .4294 | 5.94 | 17.21 | 139.67 | 415.97 | -276.29 |
| .70 | .4704 | 3.39 | 21.87 | 78.09 | 529.71 | -451.62 |
| .80 | .5365 | 1.58 | 27.22 | 34.24 | 660.52 | -626.28 |
| .90 | .6670 | .48 | 32.97 | 8.82 | 802.70 | -793.88 |
| .91 | .6872 | .42 | 33.53 | 7.31 | 816.64 | -809.33 |
| .92 | .7094 | .35 | 34.08 | 5.94 | 830.44 | -824.49 |
| .93 | .7337 | .29 | 34.63 | 4.73 | 844.07 | -839.34 |
| .94 | .7606 | .24 | 35.16 | 3.64 | 857.54 | -853.89 |
| .95 | .7903 | .19 | 35.69 | 2.69 | 870.82 | -868.12 |
| .96 | .8233 | .14 | 36.21 | 1.86 | 883.90 | -882.03 |
| .97 | .8600 | .10 | 36.71 | 1.17 | 896.77 | -895.59 |
| .98 | .9012 | .06 | 37.21 | .61 | 909.39 | -908.77 |
| .99 | .9476 | .02 | 37.69 | .21 | 921.76 | -921.54 |

Units of RT ln $\gamma_1$ are liter-atm/gm.-mole

Units of $\mu_i^E$ are cal./gm-mole.

Table 42. Polynomial Degrees in Terms of Least Sums of Squares of Deviations from the Gibbs-Duhem Equations for the System: Ethanol--Benzene.

| Temperature | Polynomial Degree of Vapor | Polynomial Degree of Total Pressure | Sums of Squares of Deviations | Value of Integral* |
|---|---|---|---|---|
| 40 | 11 | 10 | 3404 | -9.98 |
| 50 | 11 | 10 | 670 | ** |
| 60 | 11 | 11 | 2344 | -31.5 |

* $\int_0^1 (\mu_1^E - \mu_2^E)\, dx_1$

** Not calculated.

Density data were available at 46.2° C. (77) from which the corrections to the Gibbs-Duhem equation were computed. It is assumed that the values of $\Delta V$ are approximately the same at 45.0° as those at 46.2° C. Thus the last column of Table 43 indicates the magnitude of the correction terms amounts to about 15% of the computed left side of equation (67)

$$x_1 \frac{\partial \mu_1^E}{\partial x_1} + (1 - x_1) \frac{\partial \mu_2^E}{\mu x_1} = \Delta V \frac{dp}{dx_1} \qquad (67)$$

Thus, in this case of ethanol-benzene at 45.0° C., the contribution of the corrective term is less than the experimental error. Since density data for binary mixtures is relatively scarce and the corrective terms is comparatively small, it was not considered in the computations.

Table 43. Computation of $\Delta V$ and $\Delta V \frac{dp}{dx}$
For the System Ethanol (1)--Benzene (2)
at 46.2° C. and 45.0° C.

| dp/dx mm. Hg. | Wt. % EtOH | Mol Fract EtOH | $V_{ml}^{mix}$ | $\Delta V_{ml}$ | $(\Delta V \frac{dp}{dx})$ $\frac{cal}{mol}$ |
|---|---|---|---|---|---|
| 49.24 | 12.89 | 0.2006 | 85.48 | 0.293 | $.46 \times 10^{-3}$ |
| 19.235 | 20.17 | 0.2999 | 78.79 | -3.110 | $1.9 \times 10^{-3}$ |
| -28.33 | 37.14 | 0.5004 | 72.53 | -2.748 | $2.48 \times 10^{-3}$ |
| -139.00 | 57.88 | 0.6997 | 66.65 | -2.052 | $9.1 \times 10^{-3}$ |
| -488.55 | 84.16 | 0.9001 | 60.51 | -1.589 | $24.7 \times 10^{-3}$ |
| -713.45 | 94.99 | 0.9698 | 58.41 | -1.380 | $31.4 \times 10^{-3}$ |

# APPENDIX D

## SUMMARY OF TREATMENT OF BINARY SYSTEMS

In this Appendix the computations for the parameters to the standard binary activity coefficient equations for the binary systems used in this study are summarized with the results presented in sets of tables. The data for these systems were taken from the literature and the references are given in the bibliography at the end of this thesis. The binary systems are categorized according to the discussions in Chapter III of this thesis. First the non-ideal binary systems are discussed and then this is followed by a discussion of the partially miscible systems used in this work. The non-ideal miscible systems are discussed last. The parameters are calculated according to the procedures given in Chapter III.

Two ideal binary systems are discussed. Nine partially miscible binary systems and eight miscible binary systems are discussed. These nineteen binary systems are the components of the eight ternary systems presented in Chapter IV of this thesis.

Data for the physical properties were generally available in the source paper. Vapor pressure data when not available were computed by the Antoine equation using the constants from Dreisbach (101). Density data when not available in the source paper were obtained from reference (102) for the hydrocarbons and from reference (103) for other compounds. Virial coefficient data are given in Appendix B.

Ideal Binary Systems

n-heptane--cyclohexane.--Vapor-liquid equilibrium data obtained under isothermal conditions of 40 and 80° C. by Creutzen, Hasse, and Sieg (89) indicate that the excess free energy is negligibly small at these temperatures. Thus this system was considered to be ideal and the parameters of the standard equations were set equal to zero.

n-octane--isooctane.--The isobaric data of Bromiley and Quiggle (90) at 760 mm. Hg. pressure indicate that this mixture of isomers has a small excess free energy and therefore this binary system was considered to be ideal. The parameters of the standard equations were set equal to zero and no further computations were made with this system.

Partially Miscible Binary Systems

Furfural--cyclohexane.--The liquid equilibrium of the partially miscible binary system, furfural--cyclohexane, was investigated by both Bethea (17) and Pennington and Marwil (16). This system has an upper critical solution temperature of 66.2° C. Isobaric vapor-liquid equilibrium data at 760 mm. Hg. pressure have been published by Thornton and Garner (91). The temperature range of this set of data, 81.4 to 161.7 degrees, is too large to be of any extrapolative value to obtaining isothermal parameters. Using some discrete data points at a specified pressure, temperature, and vapor and liquid compositions of this binary system, a simple check of the extrapolative value of using a particular model and the reciprocal temperature relationships (40) may be obtained. For if, say the Margules model was assumed to describe the excess free energy in the homogeneous

regions, the parameters can be computed as a function of the temperature, wherever the mixture is immiscible, from the mutual solubility data, and then checked by vapor-liquid equilibrium data at temperatures above the critical solution temperature. The disadvantage of using discrete values of the vapor-liquid data is that these values may not be consistent with respect to the other data values of the vapor-liquid experiment. Some sample results are given in Table 44 testing the extrapolation of the Margules model from lower to higher temperatures. The values obtained are sufficiently close to the observed values that it is not unreasonable to state that the reciprocal temperature method along with the Margules equations describe the homogeneous regions fairly well. It should be noted that the data of reference (91) show considerable scatter which was probably due to the fact that the furfural concentrations could only be measured to one per cent accuracy.

Furfural--n-heptane.--The liquid equilibrium of the partially miscible binary system, furfural--n-heptane, was investigated by both Bethea (17) and Pennington and Marwil (16). Isobaric vapor-liquid equilibrium data at 760 mm. Hg. pressure were published by Garner (92). A check was made of the temperature dependence of the Margules model in a manner similar to that of the system, furfural--cyclohexane. The summary of the computations (given in Table 46) indicate that the reciprocal temperature and the Margules two-parameter relations are satisfactory to use in describing the homogeneous regions of this system.

Table 47 gives the values of the parameters which were used in the ternary computations.

Table 44. Summary of Computations for the Temperature Dependence of the Margules Two-Constant Model For the Binary System, Furfural (1)--Cyclohexane (2).

| Experimental Data of Reference (91): | | | |
|---|---|---|---|
| liquid composition | $x_1$ | 0.2001 | 0.6022 |
| vapor composition | $y_1$ | 0.9265 | 0.9471 |
| temperature | t° C. | 91.7 | 84.6 |
| pressure | mm. Hg. | 760.0 | 760.0 |

From a plot of $A_{12}$, $A_{21}$ versus the reciprocal of the absolute temperature, assuming a Margules two parameter model for the excess free energy, the following values are read:

| temperature, (t° C.) | 91.7 | 84.6 |
|---|---|---|
| $A_{12}$ | 0.698 | 0.761 |
| $A_{21}$ | 0.658 | 0.698 |

Using these values and assuming the vapor phase to be ideal, the following values of the vapor composition are computed and compared with the experimental data.

| Calculated furfural vapor compositions | | |
|---|---|---|
| temperature, (t° C.) | 91.7 | 84.6 |
| $y_1$ | 0.9005 | 0.941 |
| $(y_1)_{obs.} - (y_1)_{calc.}$ | 0.026 | 0.006 |

Table 45. Parameters of the Standard Equations For the System, Furfural (1)--Cyclohexane (2) As Determined from Mutual Solubility Data

| | Temperature in Degrees Centigrade | | |
|---|---|---|---|
| | 30 | 60 | 90 |
| Margules two-constant | | | |
| $A_{12}$ | 1.345 | 1.025 | 0.713 |
| $A_{21}$ | 1.016 | 0.843 | 0.672 |
| van Laar two-constant | | | |
| $A_{12}$ | 1.357 | 1.031 | 0.755 |
| $A_{21}$ | 1.025 | 0.854 | 0.705 |
| Scarchard-Hamer two-constant | | | |
| $A_{12}$ | 1.321 | 1.025 | -- |
| $A_{21}$ | 0.876 | 0.837 | -- |

Aniline--n-heptane.--The only data found for this system were mutual solubility data at 25 degrees centigrade (reference (43)), and isothermal vapor-liquid equilibrium data at 51.5° C. (reference (93)). If the mutual solubility data were also available as a function of temperature, then an excellent opportunity is afforded to determine the best correlating equation for the system by using the isothermal vapor-liquid data as a check. Considering aniline as component one and n-heptane as component two, the following parameters to the standard binary equations were obtained from the mutual solubility data of reference (43):

Table 46. Summary of Computations for the Temperature Dependence of the Margules Two Constant Model for the Binary Systems, Furfural (1)--n-heptane (2).

| | | |
|---|---|---|
| Experimental data of reference (92): | | |
| liquid composition, $x_1$ | 0.200 | 0.600 |
| vapor composition, $y_1$ | 0.868 | 0.885 |
| temperature, t° C. | 102.3 | 99.2 |
| pressure, mm. Hg. | 760.0 | 760.0 |
| Values from plot of $A_{12}$, $A_{21}$ versus reciprocal absolute temperature | | |
| $A_{12}$ | 0.789 | 0.805 |
| $A_{21}$ | 0.935 | 0.950 |
| Computed vapor composition | 0.862 | 0.863 |
| $\lvert(y_1)_{obs.} - (y_1)_{calc.}\rvert$ | 0.006 | 0.022 |

Table 47. Parameters of the Standard Equations for the System, Furfural (1)--n-heptane (2) as Determined from Mutual Solubility Data

| | Temperature in Degrees Centigrade | | |
|---|---|---|---|
| | 30 | 60 | 90 |
| Margules two-constant | | | |
| $A_{12}$ | 1.376 | 1.099 | 0.835 |
| $A_{21}$ | 1.357 | 1.168 | 0.970 |
| van Laar two-constant | | | |
| $A_{12}$ | 1.340 | 1.103 | 0.845 |
| $A_{21}$ | 1.359 | 1.167 | 0.976 |
| Scarchard-Hamer two-constant | | | |
| $A_{12}$ | 1.340 | 1.105 | -- |
| $A_{21}$ | 1.265 | 1.124 | -- |

| | $A_{12}$ | $A_{21}$ |
|---|---|---|
| Margules two-constant equation | 1.298 | 1.357 |
| van Laar two-constant equation | 1.298 | 1.357 |
| Scatchard-Hamer two constant equation | 1.276 | 1.346 |

Table 48 summarizes the parameters to the standard equations as computed from the vapor-liquid data of reference (93).

Table 48. Constants of the Standard Equations Evaluated by Least Squares for the System, Aniline (1)--n-heptane (2) at 51.5° C.

| | $A_{12}$ | $A_{21}$ | $D_{12}$ | (a) | (b) | (c) |
|---|---|---|---|---|---|---|
| Margules | | | | | | |
| 3-constant | 1.140 | 0.234 | -0.759 | 0.0008 | 0.0007 | 0.0006 |
| 2-constant | 1.143 | 0.870 | -- | 0.0009 | 0.0008 | 0.0009 |
| van Laar | | | | | | |
| 2-constant | 1.144 | 0.350 | -- | -- | 0.0008 | 0.0009 |
| Scatchard-Hamer | | | | | | |
| 3-constant | 1.140 | 0.459 | -0.404 | 0.0008 | 0.002 | 0.0001 |
| 2-constant | 1.142 | 0.0718 | -- | 0.62 | 0.4 | 0.15 |

(a) sums of squares of residuals for the ratio of activity coefficients.

(b) sums of squares of residuals for activity coefficients of component one.

(c) sums of squares of residuals for activity coefficients of component two.

Benzene--water.--This extremely immiscible binary system, has been studied by numerous investigators, among whom, Barbaudy (50) gave the most pertinent data. He conducted azeotropic distillations and determined the vapor composition in equilibrium with the two liquid phases at 69.25 degrees centigrade as well as mutual solubility data. The activity coefficients at the phase compositions were computed, assuming the vapor phase to be ideal, to be as follows,

Benzene in water-rich phase, $\gamma_{12} = 1531$ at $x_{12} = 0.00065$

water in benzene-rich phase, $\gamma_{21} = 89.9$ at $x_{21} = 0.011$

Since the concentration of the dilute components was extremely small, it was assumed that these values of the activity coefficients would suffice for the parameters in the limit, independent of the model, as suggested by equations (63) and (64).

$$\lim_{x_1 \to 0} \log \gamma_1 = 3.18 = A_{12}$$

$$\lim_{x_2 \to 0} \log \gamma_2 = 1.95 = A_{21}$$

It was furthermore assumed that these values were valid for a temperature of 60° C. for use in the computations on the ternary system, benzene-water-pyridine.

In investigations with the Margules three-constant equation, it was noted that the parameter, $D_{12}$, affected the shape of the activity coefficient curves with large values causing the curve to approach the function, $1/x$, in shape. Herington (100) had suggested that $k/x$ is the mathematical representation of the activity coefficients in a binary two-phase region. For extremely immiscible systems, the value of k approaches

unity. The value of $D_{12}$ was therefore arbitrarily increased and the shape of the curve of the activity coefficients was observed until a value of 6.20 was obtained which most nearly approximated the curve 1/x in the dilute regions.

For computations at 25° C. the parameters were determined from mutual solubility data of reference (50) to be, $A_{12} = 3.40$ and $A_{21} = 2.06$. The subscripts 1 and 2 denoted benzene and water respectively.

Chloroform--water.--This partially miscible system was studied by Reinders and deMinjer (46) who have determined the mutual solubility of this system at several temperatures and the azeotrope vapor composition at 56.12° C. Other mutual solubility data have been reported by Gibby and Hall (94). Using the azeotrope data and the mutual solubility data, the coefficients were computed at 25° C. in a manner similar to that used for the system, benzene-water. The values of the parameters were assumed to be the limiting values of the activity coefficients as given by equations (63) and (64). Thus for this system, $A_{12} = \log 731 = 2.86$ and $A_{21} = \log 89 = 1.95$, where the subscripts 1 and 2 denoted chloroform and water respectively.

Nitromethane--n-heptane.--The mutual solubility data of Kimura et al. (44) at 30 degrees centigrade was used in the computations of the two-parameter form of each of the standard equations. Considering nitromethane as component one and n-heptane as component two, the following results were obtained for the parameters to the standard equations:

| | $A_{12}$ | $A_{21}$ |
|---|---|---|
| Margules two-constant equation | 1.34 | 1.83 |
| van Laar two-constant equation | 1.36 | 1.84 |
| Scatchard-Hamer two-constant equation | 1.25 | 1.09 |

Aniline--cyclohexane.--This partially miscible system has been rather extensively studied due to the controversial nature of the "flatness" of the curve of the mutual solubility data as a function of the temperature. For the correlations, the mutual solubility data of Hunter and Brown (43) at 25° C. was used.

Roeck and Schneider (12) reported isothermal total pressure measurements for this system in the regions, which are dilute in cyclohexane, from 15 to 75° C. in five degree intervals. When the activity coefficients, computed from the total pressure measurements by equation (113) were compared to those computed by assuming a standard model, such as the Margules two-suffix model, it was found that the latter values were consistently less than the values obtained from the total pressure measurements. If equation (113) is valid

$$\gamma_{\text{cyclohexane}} = \frac{P_{\text{total}} - p_1^{\circ} x_1}{P_2^{\circ} x_2} \qquad (113)$$

to a good approximation, this would indicate that the correlation constant, $A_{21}$, is too low. ($A_{21}$ represents the value approached by the activity coefficient of cyclohexane as the mole fraction of cyclohexane tends toward zero.) Roeck and Sieg (95) published isothermal vapor-liquid equilibrium data at 40° C. for aniline concentrations in mole fractions, $x_1$, of $0.001 \leq x_1 \leq 0.271$. These data were used to obtain the parameters

to the standard binary activity coefficient equations with the results shown in Table 49.

Both sets of data clearly indicated that the activity coefficients predicted from mutual solubility data were too low and accordingly both constants should be increased. The question was to what values should they be increased. It was assumed that the total pressure measurements were reliable in both references (12) and (95) and thus by use of equation (113) for the computation of the activity coefficients, the following constants were used independent of the equational form: $A_{12} = 1.098$, $A_{21} = 0.767$.

Non-ideal Miscible Binary Systems

Ethanol--water.--The vapor-liquid equilibrium data of Jones, Schoenborn, and Colburn (96) were used to compute the constants to the standard binary equations with the results shown in Tables 53 and 54. The data of reference (96) were not quite isothermal as fluctuations of one degree centigrade were reported. It was assumed that these temperature variations were sufficiently small so that the data could be considered to be isothermal. From an examination of columns (a), (b), and (c) of Tables 50 and 51, it is concluded that the Margules 3-constant binary equations give the best fit of the data. The criterion used in these tables (and in subsequent tables) is that the sums of squares of residuals as given in columns (a), (b), and (c) of the tables be the smallest.

The vapor-liquid equilibrium data of Dornte (64) was used to compute the parameters to the standard equations at 25° C. with the results given in Table 52. From an examination of the results of this table, none of the standard equations fit the data very well.

Table 49. Constants of the Standard Equations Evaluated by Least Squares for the System, Aniline (1)--Cyclohexane (2) at 40° C.

| | $A_{12}$ | $A_{21}$ | $D_{12}$ | (a) | (b) | (c) |
|---|---|---|---|---|---|---|
| Margules | | | | | | |
| 3-constant | 1.223 | 1.395 | 1.228 | 0.0014 | 0.051 | 0.001 |
| 2-constant | 1.205 | 0.557 | --- | 0.009 | 0.070 | 0.002 |
| van Laar | | | | | | |
| 2-constant | 1.204 | 0.559 | -- | -- | 0.087 | 0.0005 |
| Scatchard-Hamer | | | | | | |
| 3-constant | 1.222 | 1.423 | 1.405 | 0.002 | 0.074 | 0.003 |
| 2-constant | 1.201 | 0.381 | -- | 0.008 | 0.080 | 0.006 |

(a) sums of squares of residuals for the ratio of activity coefficients.

(b) sums of squares of residuals for activity coefficients of component one.

(c) sums of squares of residuals for activity coefficients of component two.

Table 50. Constants of the Standard Equations Evaluated By Least Squares for the System Ethanol (1)-- Water (2) at 50° C.

| | $A_{12}$ | $A_{21}$ | $D_{12}$ | (a) | (b) | (c) |
|---|---|---|---|---|---|---|
| Margules | | | | | | |
| 3-constant | 0.686 | 0.378 | 0.171 | 0.006 | 0.0008 | 0.004 |
| 2-constant | 0.662 | 0.329 | -- | 0.007 | 0.0005 | 0.005 |
| van Laar | | | | | | |
| 2-constant | 0.766 | 0.393 | -- | -- | 0.003 | 0.29 |
| Scatchard-Hamer | | | | | | |
| 3-constant | 0.588 | 0.406 | 0.102 | 0.001 | 0.25 | 0.03 |
| 2-constant | 0.611 | 0.357 | -- | 0.006 | 0.24 | 0.03 |

(a) sums of squares of residuals for the ratios of activity coefficients.

(b) sums of squares of residuals for activity coefficients of component one.

(c) sums of squares of residuals for activity coefficients of component two.

Table 51. Constants of the Standard Equations Evaluated by Least Squares for the System Ethanol (1)-- Water (2) at 60° C.

| | $A_{12}$ | $A_{21}$ | $D_{12}$ | (a) | (b) | (c) |
|---|---|---|---|---|---|---|
| Margules | | | | | | |
| 3-constant | 0.681 | 0.366 | 0.104 | 0.008 | 0.0003 | 0.007 |
| 2-constant | 0.662 | 0.348 | -- | 0.009 | 0.0005 | 0.007 |
| van Laar | | | | | | |
| 2-constant | 0.684 | 0.367 | -- | -- | 0.0003 | 0.011 |
| Scatchard-Hamer | | | | | | |
| 3-constant | 0.616 | 0.394 | 0.119 | 0.0009 | 0.158 | 0.029 |
| 2-constant | 0.621 | 0.363 | -- | 0.009 | 0.147 | 0.037 |

(a) sums of squares of residuals for the ratio of activity coefficients.

(b) sums of squares of residuals for activity coefficients of component one.

(c) sums of squares of residuals for activity coefficients of component two.

Table 52. Constants of the Standard Equations Evaluated by Least Squares for the System Ethanol (1)--Water (2) at 25° C.

| | $A_{12}$ | $A_{21}$ | $D_{12}$ | (a) | (b) | (c) |
|---|---|---|---|---|---|---|
| Margules | | | | | | |
| 3-constant | 0.744 | 0.241 | 0.047 | 0.598 | 0.073 | 0.183 |
| 2-constant | 0.733 | 0.224 | -- | 0.600 | 0.122 | 0.180 |
| van Laar | | | | | | |
| 2-constant | 0.942 | 0.473 | -- | -- | 0.041 | 0.180 |
| Scatchard-Hamer | | | | | | |
| 3-constant | 0.684 | 0.421 | 0.127 | 0.733 | 0.061 | 0.76 |
| 2-constant | 0.880 | 0.348 | -- | 0.616 | 0.082 | 0.15 |

(a) sums of squares of residuals for the ratio of activity coefficients.

(b) sums of squares of residuals for activity coefficients of component one.

(c) sums of squares of residuals for activity coefficients of component two.

Acetone--water.--The vapor-liquid equilibrium data of Beare, et al. (65) was used in the computation of the parameters of the standard equations. The results of these computations are summarized in Table 53. From this table, it can be seen that the best fit of the data in a least squares sense appears to be attained by either of the Margules equations. A plot was made of the activity coefficients computed by the standard equations against the activity coefficients determined from the experimental data. This plot showed none of the standard equations correlated very well with the experimental data. The reason for this was that there were not many data points in the acetone-rich region. The constants to the Margules equations were adjusted to the following values,

$$A_{12} = 0.845 \qquad A_{21} = 0.64 \qquad D_{12} = 0.148$$

where the subscript one referred to acetone and two referred to water.

Acetone--chloroform.--The isothermal vapor-liquid equilibrium data of Zawidski (97) at 35.17 degrees centigrade was used in the computation of the parameters to the standard equations. It was assumed that the values of these parameters did not vary with a ten degree change in temperature for use in ternary computations at 25 degrees centigrade. The values of the parameters are given in Table 54. While the fit is not good, it can be seen from Table 57 that the Margules and Scatchard-Hamer 3-constant equations fit the data better than the other equations.

Pyridine--benzene.--The only available data for this binary system was that of Vriens and Medcalf (97) who published isobaric data at 760 mm. Hg. The temperature difference between the two pure components was 35 degrees C.

Table 53. Constants of the Standard Equations Evaluated by Least Squares for the System, Acetone (1)-- Water (2) at 25° C.

| | $A_{12}$ | $A_{21}$ | $D_{12}$ | (a) | (b) | (c) |
|---|---|---|---|---|---|---|
| Margules | | | | | | |
| 3-constant | 0.843 | 0.838 | 0.148 | 0.008 | 0.004 | 0.021 |
| 2-constant | 0.832 | 0.764 | -- | 0.010 | 0.003 | 0.021 |
| van Laar | | | | | | |
| 2-constant | 0.753 | 0.519 | -- | -- | 0.103 | 0.008 |
| Scatchard-Hamer | | | | | | |
| 3-constant | 0.707 | 0.351 | -0.244 | 1.36 | 0.910 | 0.203 |
| 2-constant | 0.618 | 0.499 | -- | 1.44 | 0.950 | 0.157 |

(a) sums of squares of residuals for the ratio of activity coefficients.

(b) sums of squares of residuals for activity coefficients of component one.

(c) sums of squares of residuals for activity coefficients of component two.

Table 54. Constants of the Standard Equations Evaluated by Least Squares for the System, Acetone (1)-- Chloroform (2) at 35.17° C.

| | $A_{12}$ | $A_{21}$ | $D_{12}$ | (a) | (b) | (c) |
|---|---|---|---|---|---|---|
| Margules | | | | | | |
| 3-constant | -0.348 | -0.205 | 0.167 | 0.050 | 0.011 | 0.038 |
| 2-constant | -0.391 | -0.241 | -- | 0.055 | 0.013 | 0.038 |
| van Laar | | | | | | |
| 2-constant | -0.348 | -0.205 | -- | -- | 0.033 | 0.046 |
| Scatchard-Hamer | | | | | | |
| 3-constant | -0.377 | -0.227 | 0.033 | 0.056 | 0.010 | 0.039 |
| 2-constant | -0.386 | -0.234 | -- | 0.062 | 0.011 | 0.040 |

(a) sums of squares of residuals for the ratio of activity coefficients.

(b) sums of squares of residuals for activity coefficients of component one.

(c) sums of squares of residuals for activity coefficients of component two.

which tends to indicate that to use this data to approximate some mean isotherm would give poor results. However, the experimental observations show that the system deviates only slightly from ideal solutions hence as an approximation it would be expected that the constants for the correlations be small.

A summary of the various correlation constants is given in Table 55. The best correlating equation in the least squares sense appears to be the Margules 3-constant equation.

Water-pyridine.--The isothermal vapor-liquid equilibrium data of Ibl et al. (63) at 30 and 50 degrees centigrade were used in the computation of the parameters of the standard equations. These results are given in Tables 56 and 57. For the ternary computations at 60 degrees centigrade, it was assumed that the parameters from the 50 degree data did not vary significantly with the temperature change. From an examination of Tables 59 and 60, it was concluded that the Margules 3-constant equations gave the better fit to the activity coefficients.

Benzene--n-heptane.--The isothermal data of Brown and Ewald (87) (88) at 60 and 80 degrees centigrade have been used for the evaluation of the parameters of the standard equations. The results are tabulated in Tables 58 and 59. The values of the parameters of the standard equations at 30 degrees centigrade were found by assuming a linear reciprocal temperature relationship. The values obtained for the two-constant van Laar equations, by this procedure were, $A_{12} = 0.127$ and $A_{21} = 0.241$.

Table 55. Constants of the Standard Equations Evaluated by Least Squares for the System Pyridine (1)-- Benzene (2) at 760 mm. Hg.

| | $A_{12}$ | $A_{21}$ | $D_{12}$ | (a) | (b) | (c) |
|---|---|---|---|---|---|---|
| Margules | | | | | | |
| 3-constant | 0.102 | 0.049 | -0.027 | 0.0010 | 0.0000 | 0.0009 |
| 2-constant | 0.108 | 0.057 | -- | 0.0001 | 0.0000 | 0.0050 |
| van Laar | | | | | | |
| 2-constant | 0.097 | 0.015 | -- | -- | 0.0005 | 0.0000 |
| Scatchard-Hamer | | | | | | |
| 3-constant | 0.137 | 0.094 | 0.151 | 0.0006 | 0.0003 | 0.0008 |
| 2-constant | 0.103 | 0.050 | -- | 0.0010 | 0.0000 | 0.0005 |

(a) sums of squares of residuals for the ratio of activity coefficients.

(b) sums of squares of residuals for activity coefficients of component one.

(c) sums of squares of residuals for activity coefficients of component two.

Table 56. Constants of the Standard Equations Evaluated by Least Squares for the System Water (1)-- Pyridine (2) at 30° C.

| | $A_{12}$ | $A_{21}$ | $D_{12}$ | (a) | (b) | (c) |
|---|---|---|---|---|---|---|
| Margules | | | | | | |
| 3-constant | 0.531 | 0.837 | 1.106 | 0.01 | 0.007 | 0.001 |
| 2-constant | 0.243 | 0.634 | -- | 0.05 | 0.02 | 0.02 |
| van Laar | | | | | | |
| 2-constant | 0.241 | 0.614 | -- | -- | 0.08 | 0.09 |
| Scatchard-Hamer | | | | | | |
| 3-constant | 0.347 | 1.022 | 0.121 | 0.007 | 0.21 | 0.19 |
| 2-constant | 0.264 | 0.958 | -- | 0.02 | 0.18 | 0.21 |

(a) sums of squares of residuals for the ratio of activity coefficients.

(b) sums of squares of residuals for activity coefficients of component one.

(c) sums of squares of residuals for activity coefficients of component two.

Table 57. Constants of the Standard Equations Evaluated by Least Squares for the System Water (1)-- Pyridine (2) at 50° C.

| | $A_{12}$ | $A_{21}$ | $D_{12}$ | (a) | (b) | (c) |
|---|---|---|---|---|---|---|
| Margules | | | | | | |
| 3-constant | 0.574 | 1.172 | 1.455 | 0.04 | 0.005 | 0.03 |
| 2-constant | 0.202 | 0.948 | -- | 0.19 | 0.03 | 0.13 |
| van Laar | | | | | | |
| 2-constant | 0.331 | 0.543 | -- | -- | 0.04 | 0.05 |
| Scatchard-Hamer | | | | | | |
| 3-constant | 0.317 | 1.297 | 0.047 | 0.02 | 0.46 | 0.17 |
| 2-constant | 0.294 | 1.286 | -- | 0.02 | 0.44 | 0.18 |

(a) sums of squares of residuals for the ratio of activity coefficients.

(b) sums of squares of residuals for activity coefficients of component one.

(c) sums of squares of residuals for activity coefficients of component two.

Table 58. Constants of the Standard Equations Evaluated by Least Squares for the System, Benzene (1)-- n-heptane (2) at 60° C.

| | $A_{12}$ | $A_{21}$ | $D_{12}$ | (a) | (b) | (c) |
|---|---|---|---|---|---|---|
| Margules | | | | | | |
| 3-constant | 0.119 | 0.207 | 0.032 | 0.008 | 0.010 | 0.008 |
| 2-constant | 0.109 | 0.198 | -- | 0.009 | 0.012 | 0.009 |
| van Laar | | | | | | |
| 2-constant | 0.116 | 0.244 | -- | -- | 0.012 | 0.008 |
| Scatchard-Hamer | | | | | | |
| 3-constant | 0.191 | 0.227 | 0.120 | 0.010 | 0.011 | 0.009 |
| 2-constant | 0.155 | 0.204 | -- | 0.012 | 0.010 | 0.010 |

(a) sums of squares of residuals for the ratio of activity coefficients.

(b) sums of squares of residuals for activity coefficients of component one.

(c) sums of squares of residuals for activity coefficients of component two.

Table 59. Constants to the Standard Equations Evaluated by Least Squares for the System, Benzene (1)-- n-heptane (2) at 80° C.

| | $A_{12}$ | $A_{21}$ | $D_{12}$ | (a) | (b) | (c) |
|---|---|---|---|---|---|---|
| Margules | | | | | | |
| 3-constant | 0.116 | 0.189 | 0.026 | 0.010 | 0.011 | 0.007 |
| 2-constant | 0.115 | 0.199 | -- | 0.011 | 0.009 | 0.008 |
| van Laar | | | | | | |
| 2-constant | 0.113 | 0.236 | -- | -- | 0.010 | 0.008 |
| Scatchard-Hamer | | | | | | |
| 3-constant | 0.146 | 0.201 | 0.011 | 0.013 | 0.011 | 0.011 |
| 2-constant | 0.135 | 0.204 | -- | 0.015 | 0.009 | 0.014 |

(a) sums of squares of residuals for the ratio of activity coefficients.

(b) sums of squares of residuals for activity coefficients of component one.

(c) sums of squares of residuals for activity coefficients of component two.

Benzene--nitromethane.--The isothermal data of Brown (99) at 45 degrees centigrade was used to evaluate the parameters of the standard equations. The parameters were assumed to be the same for 30 degrees centigrade and are summarized in Table 60.

Table 60. Constants of the Standard Equations Evaluated by Least Squares for the System, Benzene (1)-- Nitromethane (2) at 45° C.

| | $A_{12}$ | $A_{21}$ | $D_{12}$ | (a) | (b) | (c) |
|---|---|---|---|---|---|---|
| Margules | | | | | | |
| 3-constant | 0.530 | 0.603 | 0.248 | 0.006 | 0.004 | 0.008 |
| 2-constant | 0.535 | 0.556 | -- | 0.009 | 0.005 | 0.007 |
| van Laar | | | | | | |
| 2-constant | 0.535 | 0.556 | -- | 0.008 | 0.007 | 0.006 |
| Scatchard-Hamer | (not evaluated) | | | | | |

(a) sums of squares of residuals for the ratio of activity coefficients.

(b) sums of squares of residuals for activity coefficients of component one.

(c) sums of squares of residuals for activity coefficients of component two.

Ethanol--benzene.--The isothermal data of references (38) and (62) were used to evaluate the parameters of the standard equations with the results shown in Tables 61 through 64. This system is discussed in Appendix C.

Table 61. Constants of the Standard Equations Evaluated by Least Squares for the System, Ethanol (1)--Benzene (2) at 40° C.

| | $A_{12}$ | $A_{21}$ | $D_{12}$ | (a) | (b) | (c) |
|---|---|---|---|---|---|---|
| Margules | | | | | | |
| 3-constant | 1.098 | 0.745 | 0.581 | 0.007 | 0.009 | 0.001 |
| 2-constant | 1.001 | 0.668 | -- | 0.031 | 0.002 | 0.005 |
| van Laar | | | | | | |
| 2-constant | 1.010 | 0.620 | -- | -- | 0.012 | 0.017 |
| Scatchard-Hamer | | | | | | |
| 3-constant | 1.036 | 0.706 | 0.457 | 0.030 | 0.009 | 0.010 |
| 2-constant | 0.918 | 0.637 | -- | 0.032 | 0.013 | 0.011 |

(a) sums of squares of residuals for the ratio of activity coefficients.

(b) sums of squares of residuals for activity coefficients of component one.

(c) sums of squares of residuals for activity coefficients of component two.

Table 62. Constants of the Standard Equations Evaluated by Least Squares for the System, Ethanol (1)-- Benzene (2) at 45° C.

| | $A_{12}$ | $A_{21}$ | $D_{12}$ | (a) | (b) | (c) |
|---|---|---|---|---|---|---|
| Margules | | | | | | |
| 3-constant | 1.011 | 0.684 | 0.448 | 0.003 | 0.001 | 0.001 |
| 2-constant | 0.929 | 0.606 | -- | 0.015 | 0.005 | 0.003 |
| van Laar | | | | | | |
| 2-constant | 0.813 | 0.560 | -- | -- | 0.048 | 0.016 |
| Scatchard-Hamer | | | | | | |
| 3-constant | 0.955 | 0.615 | 0.378 | 0.018 | 0.009 | 0.010 |
| 2-constant | 0.849 | 0.545 | -- | 0.016 | 0.010 | 0.012 |

(a) sums of squares of residuals for the ratio of activity coefficients.

(b) sums of squares of residuals for activity coefficients of component one.

(c) sums of squares of residuals for activity coefficients of component two.

Table 63. Constants of the Standard Equation Evaluated by Least Squares for the System Ethanol (1)-- Benzene (2) at 50° C.

| | $A_{12}$ | $A_{21}$ | $D_{12}$ | (a) | (b) | (c) |
|---|---|---|---|---|---|---|
| Margules | | | | | | |
| 3-constant | 1.043 | 0.728 | 0.450 | 0.0019 | -- | -- |
| 2-constant | 0.967 | 0.665 | -- | 0.016 | -- | -- |
| van Laar | | | | | | |
| 2-constant | 1.346 | 0.636 | -- | -- | 0.099 | 0.028 |
| Scatchard-Hamer | | | | | | |
| 3-constant | 0.991 | 0.690 | 0.387 | 0.017 | -- | -- |
| 2-constant | 0.886 | 0.628 | -- | -- | -- | -- |

(a) sums of squares of residuals for the ratio of activity coefficients.

(b) sums of squares of residuals for activity coefficients of component one.

(c) sums of squares of residuals for activity coefficients of component two.

Table 64. Constants of the Standard Equations Evaluated by Least Squares for the System, Ethanol (1)-- Benzene (2) at 60° C.

| | $A_{12}$ | $A_{21}$ | $D_{12}$ | (a) | (b) | (c) |
|---|---|---|---|---|---|---|
| Margules | | | | | | |
| 3-constant | 0.986 | 0.718 | 0.339 | 0.0008 | 0.0001 | 0.0008 |
| 2-constant | 0.930 | 0.664 | -- | 0.009 | 0.007 | 0.0009 |
| van Laar | | | | | | |
| 2-constant | 1.463 | 0.654 | -- | -- | 0.255 | 0.056 |
| Scatchard-Hamer | | | | | | |
| 3-constant | 0.944 | 0.676 | 0.321 | 0.014 | 0.010 | 0.009 |
| 2-constant | 0.860 | 0.622 | -- | 0.016 | 0.013 | 0.011 |

(a) sums of squares of residuals for the ratio of activity coefficients.

(b) sums of squares of residuals for activity coefficients of component one.

(c) sums of squares of residuals for activity coefficients of component two.

# APPENDIX E

## EXPERIMENTAL WORK ON TWO TERNARY LIQUID SYSTEMS

In this Appendix, the experimental work carried out in this thesis is discussed and the experimental results are presented for the liquid-liquid equilibria of the ternary systems, nitroethane--n-octane--isooctane and nitroethane--n-octane--octene-1. The experimental results indicate that nitroethane is not a good solvent in a liquid separation process for n-octane from either isooctane or octene-1.

The ternary system, nitroethane--n-octane-isooctane was studied at 25 and 35° C., while the system nitroethane--n-octane--octene-1 was studied at 0° C. The experimental work is divided into four separate sections: description of apparatus, materials used, experimental procedure, and experimental results.

Description of apparatus.--The apparatus in which the ternary liquid samples were equilibrated was the same as that described by S.C.P. Hwa (40). The major difference was that new partition columns were constructed for the analysis of the liquid samples in the model 154-B Vapor Fractometer (manufactured by the Perkin-Elmer Corporation of Norwalk, Connecticut). Dimethyl sulfolane was found to be suitable as a stationary liquid for the separation of octene-1 from n-octane. A thirty inch partition column was prepared in the following manner:

A quantity of dimethyl sulfolane was weighed out in a small beaker. Then crushed firebrick was weighed out, such that it was 2.3 times the quantity of dimethyl sulfolane. The firebrick was of Johns-Manville C-22

type. The dimethyl sulfolane was poured into an evaporation dish and the beaker was washed out with dimethyl ether. These operations were conducted under a laboratory hood. Enough ether was added to cover the firebrick. Then the firebrick was carefully added to the dimethyl sulfolane in the evaporation dish. The mixture was heated on a water bath to evaporate the ether. When the mixture appeared to be dry it was removed from the hood and left to further dry out over night. The powder was then carefully poured into a 1/4 inch copper tube column, 30 inches in length. The procedure used was to pour a small quantity of the powder in the tube which was stopped up at one end with glass-wool, and then tap the tube on a wooden block. The procedure was repeated until the tube was filled with powder. Then the tube was bent through an angle 180° and placed in the fractometer. A slow steam of helium carrier gas was allowed to diffuse through the column for 24 hours. The column was never operated above 50° C. due to the possible elution of the stationary liquid. The dimethyl sulfolane column was operated at 40° C. with a pressure drop of 5 psig. across the column during all the runs.

For the determination of tie-lines for the system, nitroethane-n-octane--isooctane, a combination of a polyethylene glycol (carbowax 1500) and a diisodecyl phthalate partition columns was used. These columns, designated as K and A-columns, respectively, were available from the Perkin-Elmer Corporation. The vaporized sample passed through the 2 meter polyethylene glycol column first, and the nitroethane was separated from the isooctane and normal octane. Some separation occurred between the isooctane and normal octane. These vapors then entered the 30-inch diisodecyl phthalate column where all three components were further

separated. The columns were made of 1/4 inch stainless steel tubing and operated at a temperature of 108° C with a pressure drop of 22 psig. across the columns.

Material used.--The hydrocarbons used in this study were donated by the Phillips Petroleum Company, and the nitroparaffins were donated by the Commercial Solvents Corporation. The materials were used as received without further purification. The analysis for purity and determination of the refractive indices were made by Hwa (40) who concluded that the purity of the hydrocarbons and nitroethane was better than 99 weight per cent.

Experimental Procedure.--The determination of the ternary equilibrium was accomplished in two distinct steps. The binodal curve was determined, on a weight per cent basis, by the cloud point method, sometimes referred to as the synthetic method, described by Vold and Vold (41). The determination of the composition of the conjugate phases in equilibrium was accomplished by using the analytic method (41) with the analysis performed on the Vapor Fractometer. A brief description of these methods follows.

Cloud point titrations.--Solutions of known weight per cent compositions were made up from the miscible binary pairs. These solutions were of approximately 3 to 5 milliliters in volume and were placed in a 10 milliliter volumetric flask. The stoppered flask was then placed in the constant temperature bath for thirty minutes, with slight agitation, to attain thermal equilibrium. It was experimentally determined that thermal

equilibrium was attained in approximately 10 minutes, by actually measuring some samples with an Anschůtz thermometer.

In addition, tests were made on sample losses due to evaporation and it was found that losses reached one weight per cent upon standing with no stopper after six hours. With the glass stopper on, the losses reached one weight per cent in a period of 24 hours. Finally using a lightly greased glass stoppered flask covered with paraffin the losses were 0.5 weight per cent after a week. From the above tests, it was assumed that the composition change of the liquid due to evaporation was negligible during the experimental runs.

With the sample in the constant temperature bath at thermal equilibrium, the third component was added, dropwise, from a standard burrett whose tip was drawn out to decrease the drop size. The procedure was to add several drops, agitate the mixture, and then observe the solution. These operations were carried out in the constant temperature bath with the volumetric flask immersed to within a centimeter of its neck. The object of this titration procedure was to get a cloudiness in the solution.

In the precise determination of the cloud-point lies the greatest source of experimental error, since it is solely dependent upon the observer as to when the cloud-point is reached. Some solutions give a milk-white translucent appearance at the critical point and thus are easily discernable. In the case of nitroethane, normal octane, isooctane, and octene-1 mixtures, there was no distinct change of color from the clear mixture. Only the presence of finely dispersed globules or droplets of the second phase which were visible through a magnifying glass, which was used in all the cloud point determinations, denoted the fact that the

critical point had been reached.

Specifically, the first sign of the region of the cloud-point was noted by the formation of myriads of droplets when a drop of the third component was added. This second phase quickly disappeared upon agitation of the mixture. At this point one must insure that the second phase does indeed disappear and not coalesce into one drop at the bottom or at the top of the solution. This source of error was avoided by stirring the clear solution after it had been permitted to stand about 10 minutes. If the solution remains clear after the second stirring, then there is no second phase; otherwise the mixture will contain many tiny droplets. Upon the addition of another drop, the mixture may again become slightly opalescent and the above procedure is repeated until the second phase does not disappear upon agitation. It was noted that for the determinations made close to the plait point, it was difficult to discern the droplets of the second phase. For this reason, many runs were discounted because the solution was titrated past the cloud point.

The cloud point was considered to be attained when all of the following conditions were simultaneously observed:

(1) The solution consisted of a fine mist of droplets of the second phase.

(2) These droplets did not show any tendency to coalesce, although after a period of time they did coalesce to one drop and settle to the bottom or top.

(3) After the mixture of (2) became clear, it would again become dispersed with these droplets upon agitation.

When the cloud point was attained the stoppered volumetric flask was then removed from the constant temperature bath and carefully dried with absorbent paper. The bottle was then weighed, and the increase in weight due to the addition of the third component was noted.

Analysis of the conjugate phases.--Perhaps the greatest deterrent to obtaining ternary equilibrium data, for many systems, is the analysis problem. A good case in point is the difficulties presented by ternary mixtures of nitroethane, n-octane, octene-1, and isooctane. The similarities of the physical properties indicate that the usual methods of analyses by gravimetric, distillation, or refractive index methods would lead to difficulties. For these reasons it was felt that satisfactory analyses could be obtained by use of vapor chromatographic techniques.

Using the partition columns, which were previously discussed, calibration curves were made by using ternary mixtures of known compositions. The basic premise of the calibration curve was that the ratio of the peak height of one component to the sum of the peak heights of all of the components, as shown on a vapor fractogram, remained invariant with composition, operating pressure, and column temperature for any given column. Thus a plot was constructed of apparent weight fraction versus true weight fraction as determined from the ratios of peak heights on the fractogram. The peak heights on the fractogram varied on the average about five per cent, occasionally being as great as twenty per cent, for each sample. (Each sample was analyzed from three to ten times.) The ratio of the peak heights, denoting the apparent weight fractions, remained

fairly constant being reproducible to within two per cent. Thus the following maximum errors were indicated from the calibration curves for the system: nitroethane--n-octane--octene-1, for the composition range 0 - 0.2, an error of two weight per cent in the true composition; for the composition range 0.2 - 1.0, an error of eight weight per cent in the true composition. For the system: nitroethane--n-octane--octene-1; in the composition range 0 - 0.3, a maximum error of two per cent in the true composition; in the composition range 0.3 - 1.0, a maximum error of three per cent in the true composition was indicated.

The determination of the tie-lines was made by analyzing the equilibrium conjugate phases separately. From the cloud-point method, the shape of the binodal curve was obtained. From this information a mixture of approximately 150 to 200 milliliters of total volume was made up with a composition such that approximately equal volumes of both phases were present. The solution was contained in an equilibrium cell which in turn was immersed in the constant temperature bath. Approximately thirty minutes were allowed for attainment of thermal equilibrium, since it was found that in a previous work thermal equilibrium was reached after about ten minutes of stirring (40). Samples were withdrawn from the upper and lower phases by techniques previously described (40). The compositions were determined by analyzing the sample in the vapor fractometer and reading the results off the calibration curves.

The data obtained by the previously described procedures are presented in Tables 65 through 68 and Figures 28 through 30.

Table 65. Experimentally Determined Tie-line Data for the System: Nitroethane(1)--n-octane (2)--octene-1 (3) at 0° C. (in weight fractions)

| Tie-line | Upper Phase Composition<br>Lower Phase Composition | | |
|---|---|---|---|
| | $\omega_1$ | $\omega_2$ | $\omega_3$ |
| 1 | 0.079 | 0.668 | 0.253 |
| | 0.0886 | 0.083 | 0.031 |
| 2 | 0.099 | 0.515 | 0.387 |
| | 0.852 | 0.070 | 0.078 |
| 3 | 0.126 | 0.371 | 0.503 |
| | 0.812 | 0.065 | 0.123 |

Table 66. Experimentally Determined Solubility Data for the System: Nitroethane (1)--n-octane (2)--octene-1 (3) at 0° C.

| Weight Fractions of Each Component | | |
|---|---|---|
| $\omega_1$ | $\omega_2$ | $\omega_3$ |
| 0.058 | 0.942 | 0.0 |
| 0.060 | 0.840 | 0.100 |
| 0.069 | 0.731 | 0.200 |
| 0.079 | 0.621 | 0.300 |
| 0.098 | 0.502 | 0.400 |
| 0.125 | 0.375 | 0.500 |
| 0.167 | 0.250 | 0.583 |
| 0.196 | 0.204 | 0.600 |
| 0.240 | 0.155 | 0.605 |
| 0.280 | 0.120 | 0.600 |
| 0.390 | 0.060 | 0.550 |
| 0.509 | 0.041 | 0.450 |
| 0.609 | 0.041 | 0.350 |
| 0.702 | 0.048 | 0.250 |
| 0.790 | 0.060 | 0.150 |
| 0.870 | 0.080 | 0.050 |
| 0.910 | 0.090 | 0.0 |

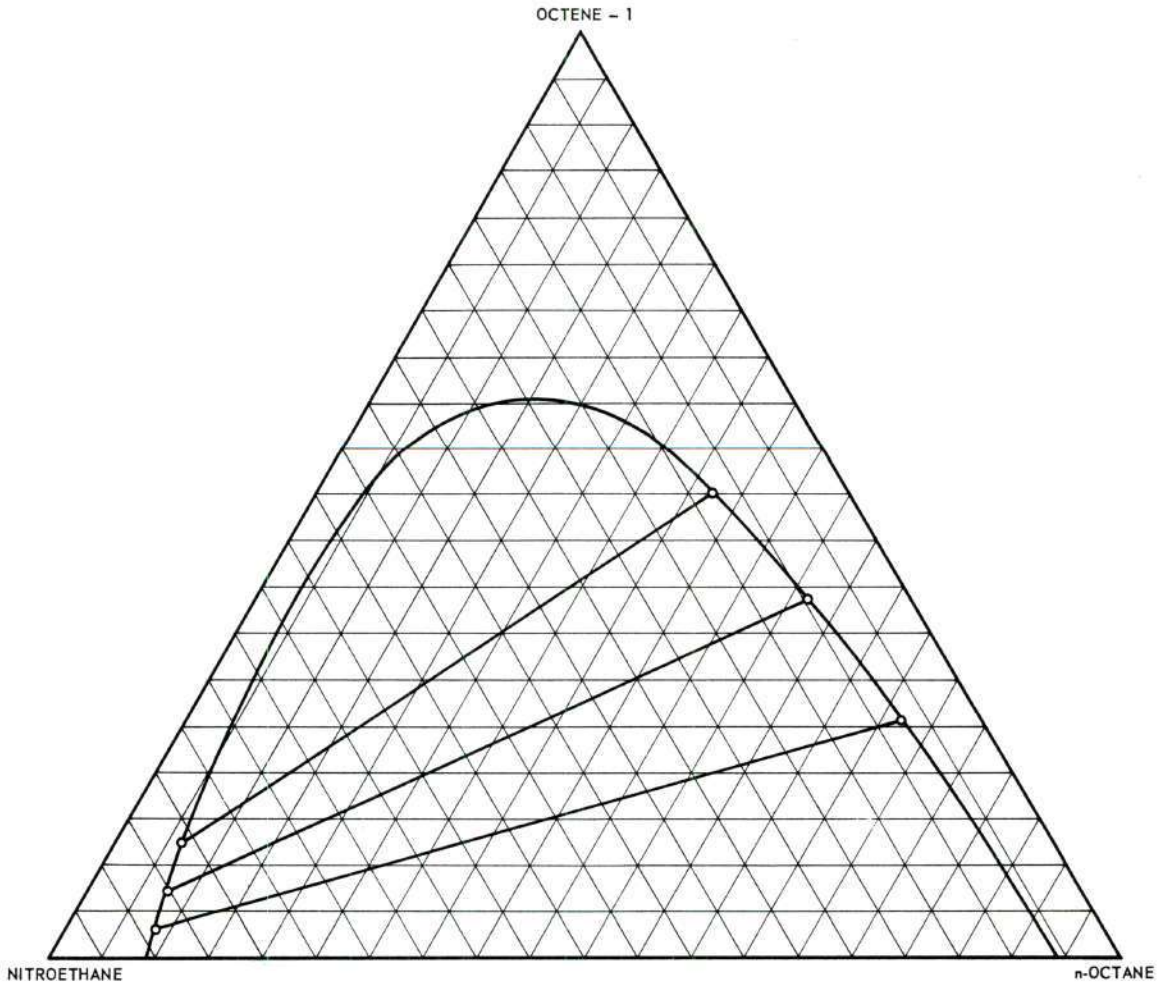


Figure 29. Experimental tie-line data for the system: nitroethane (1)--n-octane (2)--octene - 1 (3) at 0°C. in a weight percent basis.

Table 67. Experimentally Determined Tie-line Data for the System: Nitroethane (1)-- n-octane (2)--isooctane (3) at 25° C.

| Tie-line Data | Upper Phase Composition / Lower Phase Compositions | | | | | |
|---|---|---|---|---|---|---|
| | Weight Fractions | | | Mole Fractions | | |
| | $\omega_1$ | $\omega_2$ | $\omega_3$ | $x_1$ | $x_2$ | $x_3$ |
| 1 | 0.137 | 0.786 | 0.077 | 0.194 | 0.734 | 0.072 |
| | 0.826 | 0.157 | 0.017 | 0.878 | 0.110 | 0.012 |
| 2 | 0.149 | 0.519 | 0.332 | 0.210 | 0.482 | 0.308 |
| | 0.797 | 0.120 | 0.083 | 0.856 | 0.085 | 0.059 |
| 3 | 0.168 | 0.334 | 0.498 | 0.335 | 0.307 | 0.458 |
| | 0.764 | 0.085 | 0.151 | 0.831 | 0.061 | 0.108 |
| 4 | 0.224 | 0.000 | 0.776 | 0.305 | 0.000 | 0.695 |
| | 0.717 | 0.000 | 0.283 | 0.794 | 0.000 | 0.206 |
| 5 | 0.134 | 0.866 | 0.000 | 0.190 | 0.810 | 0.000 |
| | 0.828 | 0.172 | 0.000 | 0.880 | 0.120 | 0.000 |

Table 68. Experimental Results for the System Nitroethane (1)--n-octane (2)-- isooctane (3) at 35° C. in Weight Fractions.

| Tie-line | $\omega_1$ | $\omega_2$ | $\omega_3$ |
|---|---|---|---|
| 1 | 0.612 | 0.176 | 0.212 |
| | 0.319 | 0.329 | 0.362 |
| 2 | 0.637 | 0.184 | 0.179 |
| | 0.301 | 0.347 | 0.352 |
| 3 | 0.699 | 0.217 | 0.084 |
| | 0.263 | 0.528 | 0.209 |
| 4 | 0.721 | 0.233 | 0.046 |
| | 0.260 | 0.619 | 0.121 |

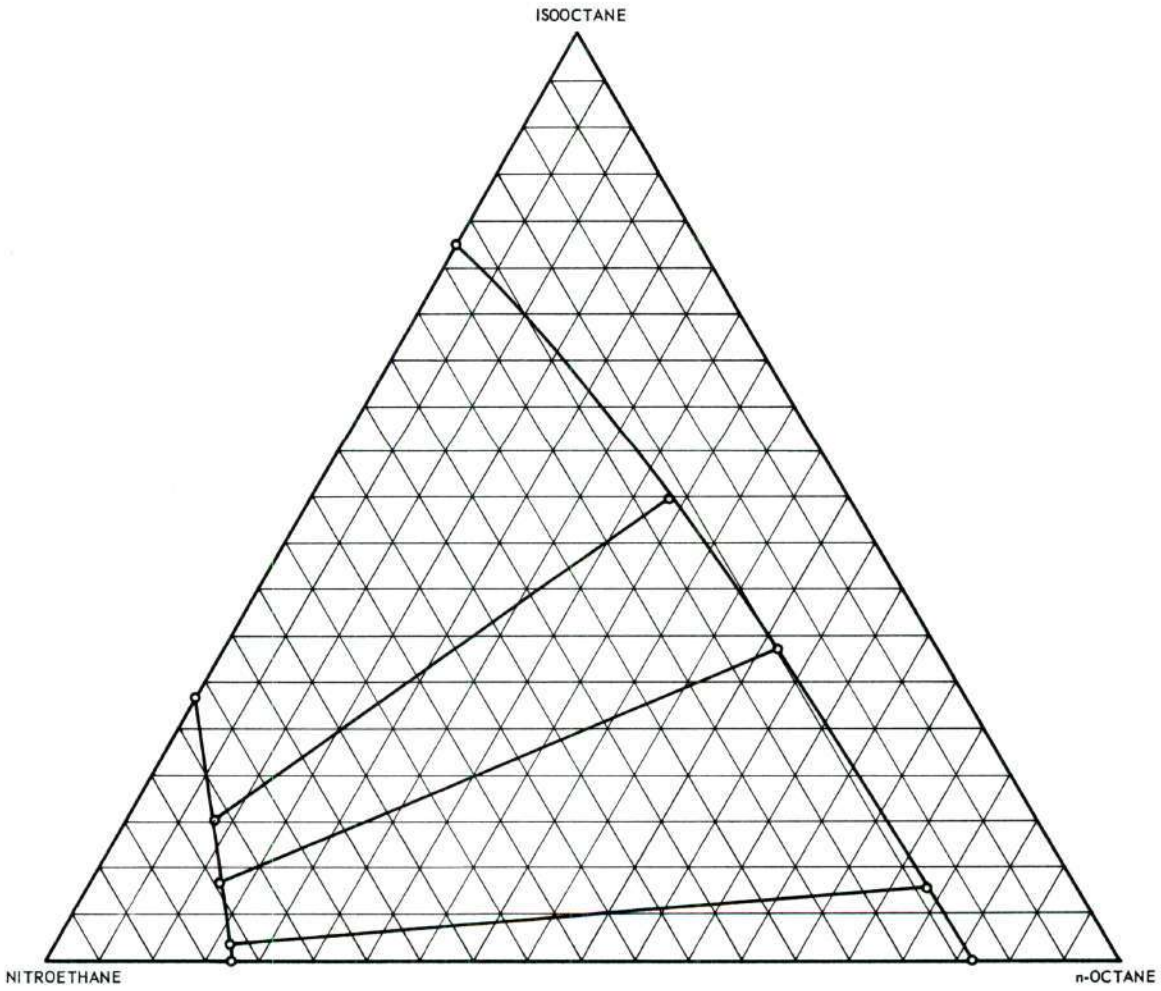


Figure 30. Experimental tie-line data for the system: nitroethane (1)--n-octane (2)--isooctane (3) at 25°C. in a weight percent basis.

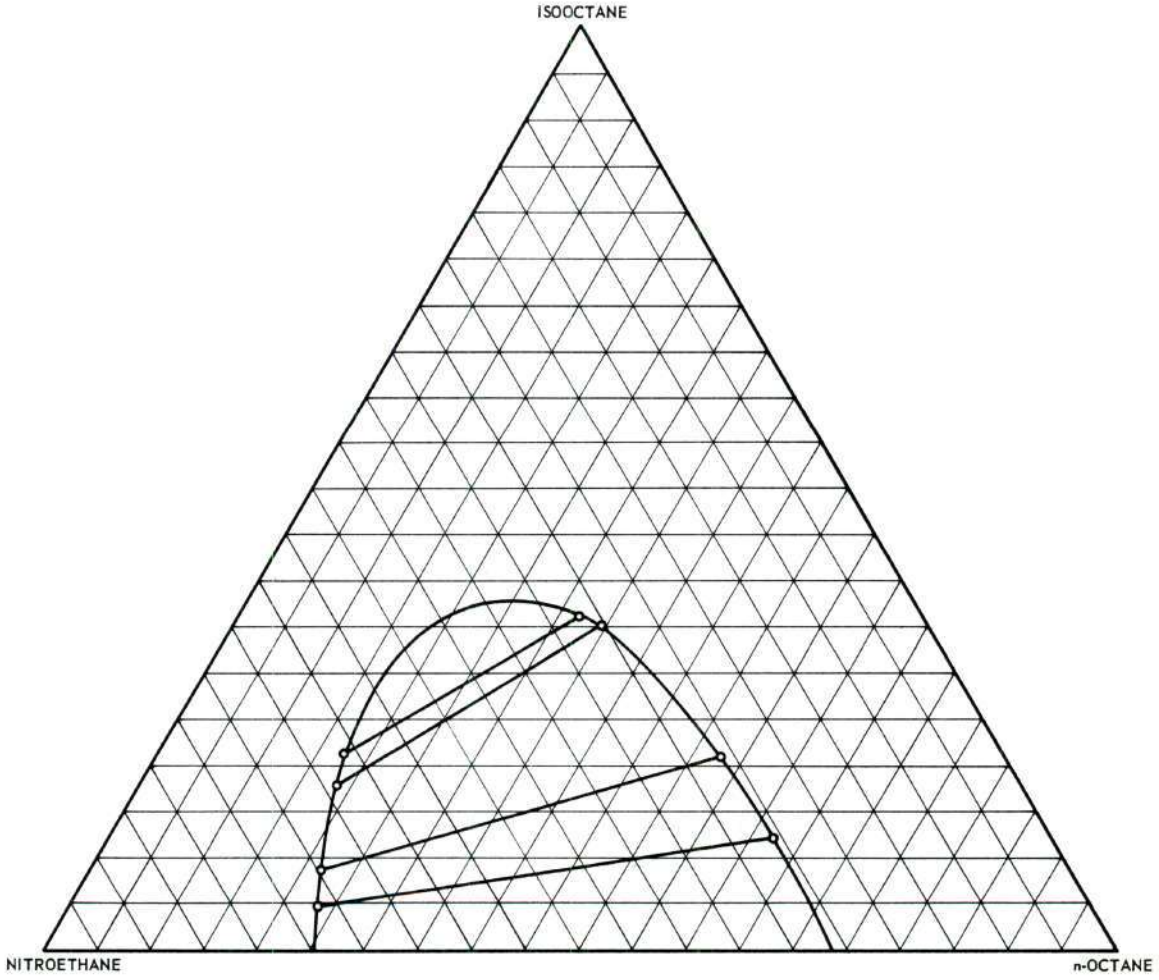


Figure 31. Experimental tie-line data for the system: nitroethane (1)--n-octane (2)--isooctane (3) at 35°C. in a weight percent basis.

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Robert Techo was born in New York City on January 1, 1931. He attended public schools there and was graduated from the Bronx High School of Science in January 1949. He entered the Georgia Institute of Technology in March 1949 and was enrolled in the Naval Reserve Officer Training Candidate program in September 1950. He received the Bachelor of Chemical Engineering degree in June 1953. On March 1953 he was commissioned Ensign, USN, and ordered to active duty on the USS Charles P. Cecil (DDR-835). He served as Engineering Officer of that ship from March 1955 until his release from active duty in March 1956. He entered graduate school at the Georgia Institute of Technology in March 1956 and received the degree of Master of Science in Chemical Engineering in June 1958. His M.S. thesis, entitled A Bibliography of Thermodynamic Networks for Pure Substances, was done under the supervision of Dr. W. T. Ziegler. He was awarded the Phillips Petroleum Fellowship for the academic year 1958-59. From July 1959 to the present he was employed by the Rich Electronic Computer Center at Georgia Tech. Part of this employment was supported by a grant from the National Science Foundation through the Rich Electronic Computer Center and involved a study of the computer aspects of liquid-liquid equilibrium computations. He is at the present time also a Lecturer in the School of Mathematics at Georgia Tech.

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